

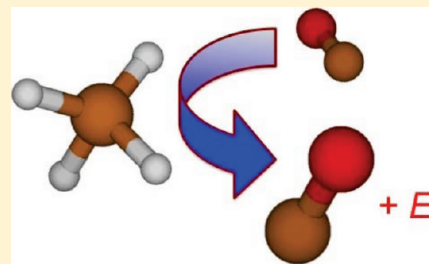
Theoretical Unimolecular Kinetics for $\text{CH}_4 + \text{M} \rightleftharpoons \text{CH}_3 + \text{H} + \text{M}$ in Eight Baths, $\text{M} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{H}_2, \text{N}_2, \text{CO},$ and CH_4

Ahren W. Jasper* and James A. Miller

Combustion Research Facility, Sandia National Laboratories, P.O. Box 969, Livermore, California 94551-0969, United States

S Supporting Information

ABSTRACT: Ensembles of classical trajectories are used to study collisional energy transfer in highly vibrationally excited CH_4 for eight bath gases. Several simplifying assumptions for the $\text{CH}_4 + \text{M}$ interaction potential energy surface are tested against full dimensional direct dynamics trajectory calculations for $\text{M} = \text{He}, \text{Ne},$ and H_2 . The calculated energy transfer averages are confirmed to be sensitive to the shape of the repulsive wall of the intermolecular potential, with an exponential repulsive wall required for quantitative predictions. For the diatomic baths, the usual “separable pairwise” approximation for the interaction potential is unable to describe the orientation dependence of the interaction potential accurately, and the ambiguity in the resulting parametrizations contributes an additional uncertainty to the predicted energy transfer averages of 20–40%. On the other hand, the energy transfer averages are shown to be insensitive to the level of theory used to describe the intramolecular CH_4 potential, with a computationally efficient semiempirical tight binding potential for hydrocarbons performing equally well as an MP2 potential. The relative collisional energy transfer efficiencies of the eight bath gases are discussed and shown to be a function of temperature. The ensemble-averaged energy transferred in deactivating collisions $\langle \Delta E_d \rangle$ for each bath is used to parametrize a single-exponential-down model for collisional energy transfer in master equation calculations. The predicted decomposition rate coefficients for CH_4 agree well with available experimental rate coefficients for $\text{M} = \text{He}, \text{Ar}, \text{Kr},$ and CH_4 . The effect of vibrational anharmonicity on the predicted rate coefficients is considered briefly.



I. INTRODUCTION

Collisions with bath gas molecules play an important role in controlling the rates of unimolecular and chemically activated reactions. In the low-pressure limit of a unimolecular dissociation,¹ the reaction occurs much faster than collisions with the bath gas, so that every activated molecule has enough time to react before being deactivated. The low-pressure unimolecular rate coefficient is therefore proportional to the rate of activating collisions and to the pressure. (This simple picture may be complicated by tunneling reactions below threshold and by long-lived metastable states above threshold.) At intermediate pressures, unimolecular and chemically activated rates are determined by a competition between intermolecular collisional energy transfer and intramolecular forces.

Pressure-dependent kinetics may be characterized theoretically using the master equation (ME),^{2–4} which, in general, describes the time dependence of the microcanonical state populations of the reactants, products, and intermediates. ME calculations require knowledge of the intramolecular potential energy surface (dissociation energies, isomerization barriers, vibrational frequencies, etc.), which may be obtained with known uncertainties from electronic structure calculations. Likewise, the required intramolecular isomerization and capture rate coefficients may be calculated using transition state theory,⁵ with well-validated, predictive strategies for treating barrierless reactions, tunneling, and so on. In contrast, the models used in ME calculations for describing collisional energy transfer remain highly empirical.

In principle, predictive theoretical models for pressure-dependent kinetics require detailed knowledge of collision rates and efficiencies as a function of the total energy and total angular momentum of the excited complex. In practice, several simplifying assumptions are often made when modeling energy transfer in the context of the ME. One strategy⁴ for constructing and solving the ME involves the following assumptions about energy transfer:

- (1) The dependence on the initial rotational state of the energized complex is neglected.^{6,7}
- (2) The energy transfer function is assumed to be dependent on the amount of energy transferred but independent of the initial and final energies individually.
- (3) The probability distribution of energy transferred per deactivating collision is assumed to be exponential,¹ with the activating probability distribution determined from detailed balance. This approximation is called the “single-exponential-down” model.

None of these assumptions is supported by classical trajectory studies of energy transfer. In fact, energy transfer has been shown to be enhanced by rotational^{8–11} and vibrational^{8,11–14} excitation, with biexponential (or, equivalently, long-tail) probability distributions.^{8,11,14} Although quantitative comparisons can be

Received: January 3, 2011

Revised: April 5, 2011

difficult, these results generally agree with those obtained from the extensive experimental energy transfer literature.^{15–18}

These assumptions arise in part due to a lack of detailed information about the energy transfer function (assumptions 2 and 3) and in part to facilitate the solution of the ME (assumption 1). More sophisticated treatments of the initial energy dependence and of the probability distribution for energy transfer can be readily included in ME calculations, but such treatments are often not needed. Barker and Weston¹¹ have recently used classical trajectories to parametrize an energy transfer function that includes angular momentum dependence and that does not assume the separability of total energy and total angular momentum; ME calculations employing such a so-called “two-dimensional” energy transfer function remain rare, however.

When the present set of assumptions is used, the single-exponential-down model requires a single parameter α , which can be associated with the average energy transferred in deactivating collisions¹ $\langle \Delta E_d \rangle$. This parameter is often further assumed to be a function of temperature and written

$$\alpha(T) = \alpha_{300}(T/300 \text{ K})^n \quad (1)$$

Almost every ME prediction of unimolecular and chemically activated rate coefficients to date has used empirically determined or estimated α_{300} and n . Fortunately, the predicted rate coefficients are often not overly sensitive to these parameters, and similar empirically determined values are typically obtained for similar species, with $\alpha_{300} = 50\text{--}300 \text{ cm}^{-1}$ and $n \approx 1$.

Occasionally, however, surprising values of α_{300} and n are required to reproduce experimental data. For example, in a recent study of CH_3Cl decomposition¹⁹ the values of α required to fit the results of an ME calculation empirically to measured decomposition rate coefficients were found to be four times as large as those obtained in a similar study of CH_4 . As another example, low-pressure decomposition rate coefficients for water were calculated²⁰ using the ME approach, and a relatively weak temperature dependence in α ($n = 0.4\text{--}0.5$) was required to fit the experimental data. It is unclear whether these atypical values of α reflect genuinely “unusual” energy transfer dynamics or instead indicate errors in the measured rate coefficients or are compensating for errors in other parts of the calculation. The transferability of empirically determined energy transfer parameters is also uncertain. For example, when the results of ME calculations²¹ fit to measured ethane decomposition rate coefficients above 1500 K were extrapolated to lower temperatures, the theoretical rate coefficients were found to overpredict low temperature experimental values. Rate coefficients over the entire temperature range could be fit by decreasing α_{300} from 120 to 45 cm^{-1} and increasing n from 0.9 to 1.4.²²

A strategy for obtaining predictive pressure-dependent unimolecular rate coefficients is clearly desirable. In the context of the ME and assumptions 1–3 outlined above, such a strategy requires a method for predicting $\alpha(T)$. We recently reported¹⁰ the results of ME calculations of rate coefficients for the $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$ reaction in He using the energy transfer model discussed above, with the parameters α_{300} and n calculated by direct classical trajectories. Errors in the predicted energy transfer dynamics were minimized by using an ab initio potential energy surface and by selecting the trajectories’ initial conditions and ensemble averages to be consistent with the ME model. The resulting parameter-free rate-coefficient predictions were shown to be in good agreement with measured values.

Here we extend our previous study of CH_4 decomposition in He^{10} to include heavier atomic baths (Ne, Ar, and Kr), three diatomic baths (H_2 , N_2 , and CO), and one polyatomic bath (CH_4). The main goal of this work is to predict $\alpha(T)$ theoretically for these baths using classical trajectories.

As mentioned above, numerous classical trajectory studies of energy transfer have been carried out, and these studies typically invalidate assumptions 1–3. Despite the demonstrated invalidity of these approximations, ME calculations employing these assumptions have nonetheless been used to successfully model a wide variety of unimolecular and chemically activated reactions. It may be that the empirically determined values for α compensate for errors in the energy transfer model. Alternatively, it is possible that the assumptions outlined above do not introduce significant errors into the resulting predicted rate coefficients for some reactions. Assumption 2 may be motivated by noting that low pressure rate coefficients are sensitive only to those collisions involving systems with energies close to the dissociation threshold.¹ Several energy transfer models were previously tested for CH_4 dissociation,⁷ where it was shown that assumption 3 had negligible effects on the predicted kinetics; this result is likely true for any simple dissociation reaction (i.e., for any reaction with only one molecular complex and one set of products). Finally, the results of the classical trajectory dynamics themselves can be uncertain due to the approximate potential energy surfaces and initial conditions employed. Another major goal of the present work is therefore to quantify the errors associated with the classical trajectory calculations, with a particular emphasis on how the description of the potential energy surface affects the computed energy transfer averages. The results of direct dynamics trajectory ensembles are reported here for four baths: He, Ne, H_2 , and CH_4 . The results for $\text{M} = \text{He}$, Ne, and H_2 are used to test the accuracy of simpler, more efficient analytic and semiempirical descriptions of the potential energy surface. Specifically, the accuracy of representing of the interaction potential as separable from the intramolecular CH_4 potential energy surface and as a sum of fitted pairwise interactions is tested. This separable pairwise approximation is almost always employed in energy transfer studies using classical trajectories.

Classical trajectories have been used previously to study trends in collisional energy transfer efficiencies with respect to the bath gas.^{14,23–25} In these studies, He has generally been found to be the most efficient atomic collider in contrast to some experimental work.^{26,27} Gilbert²³ carefully considered several sources of error in the trajectory calculations for $\text{M} = \text{He}$, and the discrepancy between the experimental and trajectory results was ultimately attributed to approximations in the interaction potential energy surfaces used in the trajectory calculations. Gilbert’s analysis further motivates the present tests of the accuracy of typical approximations to the interaction potential that are often used in trajectory studies.

Finally, the present predicted values for $\alpha(T)$ for eight bath gases are used in parameter-free ME calculations for $\text{CH}_4 (+\text{M}) \rightleftharpoons \text{CH}_3 + \text{H} (+\text{M})$. The relative efficiencies of the bath gases are discussed, and the predicted decomposition rate coefficients are compared with available experimental rate coefficients for $\text{M} = \text{He}$, Ar, Kr, and CH_4 . The low-pressure experimental data for Ar and Kr, in particular, provide a more direct test of the energy transfer models and parametrizations than the falloff data previously considered¹⁰ for $\text{M} = \text{He}$.

In section II, the present implementation and solution of the ME is briefly discussed, and the direct dynamics and separable pairwise trajectory calculations are described in detail.

In section III, validation studies of the approximate potential energy surfaces are presented, a comparison of the predicted bath gas efficiencies is made, and decomposition rate coefficients for CH₄ in He, Ar, Kr, and CH₄ are compared with experimental ones. Section IV summarizes our conclusions.

II. THEORY

II.A. Master Equation Analysis. The ME formalism employed here has been described in detail elsewhere.^{4,7} Briefly, for an irreversible unimolecular reaction, the ME governing the microcanonical population densities $n(E, J)$ of the reactant complex (CH₄ in the present work) is

$$\dot{n}(E, J, t) = \sum_{J'} \int_0^\infty dE' R(E, J; E', J') n(E', J', t) n_M - \sum_{J'} \int_0^\infty dE' R(E', J'; E, J) n(E, J, t) n_M - k(E, J) n(E, J, t) \quad (2)$$

where E and J are the total energy and angular momentum characterizing the energy “grain”¹ or “state” (E, J), $R(E, J; E', J')$ is the second-order collisional energy transfer rate coefficient for a transition from the state (E', J') to another state (E, J), $k(E, J)$ is the microcanonical dissociation rate, and n_M is the concentration of the bath gas. Note that R is implicitly a function of the temperature T and of the identity of the bath gas.

The energy transfer rate coefficient is often written as the product of a total collision rate coefficient

$$Z(E', J') \equiv \sum_J \int_0^\infty dE R(E, J; E', J') \quad (3)$$

and an energy transfer probability

$$P(E, J; E', J') \equiv R(E, J; E', J') / Z(E', J') \quad (4)$$

such that P is normalized when integrating and summing over final states (E, J).

At low and intermediate pressures, the solution of the two-dimensional (E, J) ME in eq 2 requires the detailed energy transfer function $R(E, J; E', J')$. Knowledge of the dependence of R on E, J, E' and J' is typically not available. Furthermore, it can be difficult, in general, to enforce the detailed balance condition

$$R(E', J'; E, J) g(E, J) = R(E, J; E', J') g(E', J') \quad (5)$$

where $g(E, J)$ is the thermally equilibrated population of the state (E, J), while including the rotational dependence of R . To facilitate the solution of the ME, we assume that the energy transfer rate coefficient is independent of the initial rotational state^{6,7} (assumption 1 from the Introduction), that is,

$$R(E, J; E', J') = R(E; E') \varphi(E, J) \quad (6)$$

With this substitution, eq 2 becomes

$$\dot{\bar{n}}(E, t) = \int_0^\infty dE' R(E; E') \bar{n}(E', t) n_M - \int_0^\infty dE' R(E'; E) \bar{n}(E, t) n_M - \bar{k}(E) \bar{n}(E, t) \quad (7)$$

if

$$\sum_J \varphi(E, J) = 1 \quad (8)$$

where

$$\bar{n}(E, t) \equiv \sum_J n(E, J, t) \quad (9)$$

$$\bar{k}(E) \equiv \sum_J k(E, J) n(E, J, t) / \bar{n}(E, t) \quad (10)$$

Equation 7 has the form of a one-dimensional ME, except that \bar{k} depends on $n(E, J)$, which in turn requires the full solution to the two-dimensional ME. Equation 10 can be written⁴

$$\bar{k}(E) = \sum_J k(E, J) y(E, J) / \sum_J y(E, J) \quad (11)$$

with

$$y(E, J) = \frac{\varphi(E, J)}{Z(E, J) + k(E, J) - k_{T,p}} \quad (12)$$

Assuming $k_{T,p}$ is small and can be neglected when evaluating eq 12 decouples the calculation of \bar{k} from the solution of eq 7.^{6,7}

Detailed balance is enforced by writing $R(E, E')$ as

$$R(E, E') = ZP(E, E') \quad (13)$$

assuming Z is an energy-independent Lennard-Jones collision rate, and using the exponential down model (assumptions 2 and 3 from the Introduction)

$$P(E, E') = A \exp(-(E' - E)/\alpha) \quad E < E' \quad (14)$$

and an empirical model⁶ for rotational dependence

$$\varphi(E, J) = (2J + 1) \rho(E, J) / \rho(E) \quad (15)$$

$$\rho(E) = \sum_J (2J + 1) \rho(E, J) \quad (16)$$

where $\rho(E, J)$ is the state density. (Note that for the spherical top CH₄ there is an additional factor of $(2J + 1)$ degeneracy due to the quantum number τ . This degeneracy is included in ρ so that the present equations are suitable for the more general case of an asymmetric top.) The parameter A in eq 14 is chosen such that $P(E, E')$ is normalized, with the activating wing of $P(E, E')$ determined from detailed balance

$$P(E', E) g(E) = P(E, E') g(E') \quad (17)$$

The single remaining parameter α can be shown to be equal to the average energy transferred in deactivating collisions when α is much less than the threshold energy for dissociation (which is typically the case) for the exponential distribution of $\Delta E = |E - E'|$ in eq 14.¹ Note that the average energy in deactivating collisions is a function of the initial energy¹ E' and that this energy dependence has been neglected. When calculating α with classical trajectories, we choose E' to be close to the dissociation threshold, as discussed below. The parameter α is a function of temperature^{1,7,28} and is often written as in eq 1.

Table 1. Lennard-Jones Collision Frequency Parameters^a

	σ , Å	ϵ , cm ⁻¹
CH ₄	3.746	98.28
He	2.576	7.089
Ne	2.749	24.74
Ar	3.330	94.87
Kr	3.679	122.3
H ₂	2.920	26.41
N ₂	3.681	67.89
CO	3.705	71.49

^a Ref 33.

In the high pressure limit, thermal equilibria are maintained, and the solution to the ME can be written

$$\begin{aligned}
 k_{T,p}^{\infty} &= \sum_J \int_0^{\infty} dE k(E,J) g(E,J) \\
 &= \sum_J \int_0^{\infty} dE k(E,J) (2J+1) \rho(E,J) \exp(-E/k_B T) / Q
 \end{aligned} \quad (18)$$

where Q is the partition function for the dissociating molecule

$$Q \equiv \sum_J \int_0^{\infty} dE (2J+1) \rho(E,J) \exp(-E/k_B T) \quad (19)$$

Equation 18 is the usual unimolecular transition state theory rate expression. Collisional energy transfer does not appear explicitly in the high-pressure limit rate coefficient expression; instead, collisions are implicitly assumed to be sufficiently fast and energetic to maintain the thermal populations $g(E,J)$ despite the reaction potentially perturbing these equilibria.

The low-pressure limit rate coefficient can be written¹

$$k_{T,p}^0 = \sum_{J'} \int_0^{E_{J'}} dE' \sum_J \int_{E_J}^{\infty} dE R(E,J; E', J') x(E', J') \quad (20)$$

where E_J is the rotationally adiabatic threshold energy for the total angular momentum J and $x(E,J)$ are the normalized steady state solutions of the ME, which are approximately proportional to $\rho(E,J)$ at low pressures.¹ The low-pressure-limit rate coefficient is determined by collisions promoting the system from some state below threshold to some state above threshold. Clearly, only states with energies within $\sim \alpha$ of the dissociation threshold can contribute to the low pressure unimolecular rate coefficient. This observation justifies the neglect of the dependence of α on E' for simple dissociation reactions and motivates our choice of E' to be close to the dissociation threshold. At falloff pressures, energy transfer over a wider energy range contributes to the dissociation, but the kinetic effect of the dependence of α on E' is mitigated by the approach to the high pressure limit, which is independent of α .

In the present ME calculations for $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$, the microcanonical dissociation rate coefficient $k(E,J)$ were taken from the $\text{CH}_3 + \text{H}$ direct VRC-TST capture rate calculation of ref 29 transformed via the equilibrium constant, which was calculated as the ratio of rigid-rotor, harmonic-oscillator (RRHO) partition functions. The RRHO partition functions were calculated using experimental values³⁰ for the zero-point

Table 2. Errors for Several Low-Level Direct Dynamics and Approximate Interaction Potential Energy Surfaces Relative to Counterpoise Corrected QCISD(T)/CBS Energies

M	PES ^a	Direct Dynamics		
		ϵ_{min} , cm ⁻¹	ϵ_{rel} , %	ϵ_{rep} , Å
He	MP2	3.9	13.9	0.04
Ne	MP2	4.9	7.9	0.02
CH ₄	MP2	10.3	5.4	0.01
H ₂	MP2	24.3	23.7	0.04
	SAC	11.1	10.8	0.02

M	V_{M-T}	Separable Pairwise		
		ϵ_{min} , cm ⁻¹	ϵ_{rel} , %	ϵ_{rep} , Å
He	exp/6	1.1	4.0	0.04
	LJ-A	1.8	6.5	0.26
	LJ-B	7.0	25.0	0.13
Ne	exp/6	4.0	6.5	0.03
Ar	exp/6	6.8	4.9	0.03
Kr	exp/6	7.8	4.8	0.03
H ₂	exp/6 RP	24.8	24.9	0.06
	exp/6 R	30.9	24.2	0.12
	exp/6 P	25.6	30.1	0.10
N ₂	exp/6 RP	39.5	24.7	0.04
	exp/6 R	24.9	15.5	0.03
	exp/6 P	23.1	14.4	0.04
CO	exp/6 RP	36.3	20.5	0.12
	exp/6 R O-in	45.4	25.7	0.18
	exp/6 R C-in	35.0	19.8	0.41
	exp/6 P	68.5	38.7	0.24

^aThe aug'-cc-pVDZ basis set was used for the MP2 and SAC calculations.

inclusive dissociation energy (36168 cm⁻¹), the frequencies of CH₄ (3019, 2917, 1543, and 1306 cm⁻¹), the rotational constant of CH₄ (5.24 cm⁻¹), the frequencies of CH₃ (3161, 3004, 1396, and 606 cm⁻¹), and the rotational constants of CH₃ (9.58 and 4.74 cm⁻¹). (A one-dimensional anharmonic correction to the RRHO partition functions for the umbrella mode of CH₃ based on the calculated potential in ref 31 was considered; this correction had a very small effect on the predicted rate coefficients.)

Lennard-Jones parameters^{32,33} (summarized in Table 1) were used to compute the $\text{CH}_4 + \text{M}$ collision rates Z using the usual combining rules; the arithmetic mean of the collision radii and the geometric mean of the well depths were used. Classical trajectories were used to calculate $\alpha(T)$, as described in detail in section II.B. ME calculations were carried out using Variflex.³⁴ Association rate coefficients (k_a) were obtained by converting the dissociation rate coefficients via the calculated equilibrium constant.

II.B. Classical Trajectories. Direct Dynamics. Full-dimensional direct dynamics trajectory calculations were used to study energy transfer for the He, Ne, H₂, and CH₄ baths. These simulations included thousands of trajectories for each bath gas, and thousands of gradient evaluations were required for each trajectory. The level of electron correlation and the size of the basis set that could be used to describe the molecular forces in the direct dynamics trajectory calculations were therefore limited

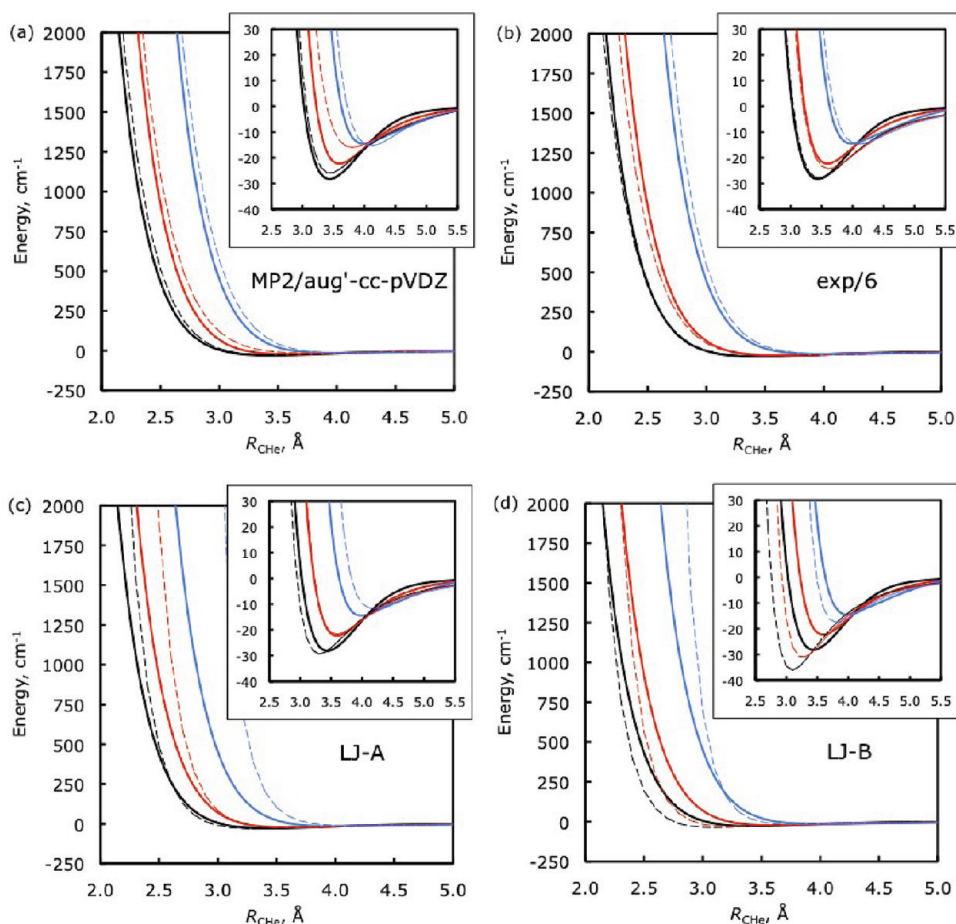


Figure 1. $\text{CH}_4 + \text{He}$ interaction potential for face (black), edge (red), and vertex (blue) approaches. The solid lines in all four panels are QCISD(T)/CBS energies, and the dashed lines are (a) MP2/aug'-cc-pVDZ, (b) exp/6, (c) LJ-A, and (d) LJ-B energies. The insets highlight the van der Waals well.

to methods that could affordably be used for $\sim 10^7$ gradient calculations. The strategy adopted here was to use high-level ab initio calculations (counterpoise corrected QCISD(T) calculations with complete basis set (CBS) extrapolations based on the aug-cc-pVDZ and aug-cc-pVTZ basis sets) to evaluate the accuracy of lower-level quantum chemistry methods with efficiencies suitable for direct dynamics.

The accuracies of the lower-level direct dynamics potential energy surfaces were evaluated by considering interaction energies along three to nine $\text{CH}_4\text{--M}$ approaches and calculating the following errors relative to the QCISD(T)/CBS energies: ϵ_{\min} , the root-mean-squared error in the minimum energy along each approach; ϵ_{rep} , the root-mean-squared error in the center of mass separations at 2000 cm^{-1} up the repulsive wall along each approach; and $\epsilon_{\text{rel}} \equiv \epsilon_{\min}/V_{\min}$, a relative error in the well depth, where V_{\min} is the QCISD(T)/CBS van der Waals well depth for the most favorable approach. For the atomic baths, three approaches of M to CH_4 (fixed at its classical equilibrium geometry) were considered, with “face” and “vertex” denoting approaches along a C_3 axis with M equidistant from the nearest 3 and 1 H atoms on CH_4 , respectively, and “edge” denoting a C_2 approach bisecting two H atoms on CH_4 . Figures representing these approaches are given as Supporting Information. For the diatomic baths, face, vertex, and edge approaches of the center of mass of M to CH_4 were considered for two or three orientations of the bath gas for a total of six or nine approaches. For $\text{M} = \text{CH}_4$,

three approaches were considered: a face–face approach, a face–vertex approach, and a vertex–vertex approach. The errors in the direct dynamics and approximate potential energy surfaces discussed throughout section II.B are summarized in Table 2; figures comparing QCISD(T)/CBS interaction energies with the lower-level direct dynamics and approximate potential energy surfaces for all the bath gases considered here are provided as Supporting Information.

A direct dynamics trajectory study of energy transfer in CH_4 for $\text{M} = \text{He}$ was previously reported¹⁰ using the MP2/aug'-cc-pVDZ potential energy surface, where it was shown to predict interaction energies in good agreement with QCISD(T)/CBS energies, as reproduced in Figure 1a. The “aug'” notation³⁵ indicates a modification of the usual augmented Dunning basis sets where the diffuse functions are not included for H. For He, the average error in the well depth ϵ_{\min} for the MP2/aug'-cc-pVDZ method is only 4 cm^{-1} , and the error in the repulsive wall distance ϵ_{rep} is 0.04 Å . The accuracy of the MP2/aug'-cc-pVDZ method was further tested here for $\text{M} = \text{Ne}$, CH_4 , and H_2 . Agreement between the MP2/aug'-cc-pVDZ and QCISD(T)/CBS interaction energies is excellent for Ne ($\epsilon_{\min} = 5\text{ cm}^{-1}$; $\epsilon_{\text{rep}} = 0.02\text{ Å}$) and CH_4 ($\epsilon_{\min} = 10\text{ cm}^{-1}$; $\epsilon_{\text{rep}} = 0.01\text{ Å}$). For $\text{M} = \text{H}_2$, interaction energies were considered where the bath gas was oriented either radially (i.e., along the direction of the approach) or perpendicular to the direction of approach for a total of six $\text{CH}_4\text{--M}$ approaches. The MP2/aug'-cc-pVDZ method performs

less well for H₂ than for He, Ne, and CH₄, although the agreement is still good with $\epsilon_{\min} = 24 \text{ cm}^{-1}$ and $\epsilon_{\text{rep}} = 0.04 \text{ \AA}$. A simple empirical improvement to the MP2/aug'-cc-pVDZ potential for M = H₂ was made by "scaling all correlation"³⁶ (SAC), where $E_{\text{SAC}} = E_{\text{HF}} + (E_{\text{MP2}} - E_{\text{HF}})/F$, and E_{MP2} and E_{HF} are MP2/aug'-cc-pVDZ and HF/aug'-cc-pVDZ energies, respectively; the parameter $F = 0.8$ was empirically optimized to fit the QCISD(T)/CBS interaction energies. With this adjustment, the SAC method more accurately describes the depth of the van der Waals well and the range of the repulsive wall ($\epsilon_{\min} = 11 \text{ cm}^{-1}$ and $\epsilon_{\text{rep}} = 0.02 \text{ \AA}$). These errors are reduced by a factor of 2 relative to those for the unscaled MP2 surface; the difference in the computational costs of the MP2 and SAC methods is negligible.

The use of the MP2 and SAC methods with double- ζ basis sets is a compromise between accuracy and computational efficiency. Furthermore, the good accuracy for the MP2/aug'-cc-pVDZ method discussed above is likely due to a cancellation of errors arising from the incomplete treatment of electron correlation and the use of finite basis sets. The present procedure, in fact, relies upon the accidental accuracy of a low level quantum chemistry method that has been validated against accurate QCISD(T)/CBS energies. For example, the MP2 interaction potentials are not converged with respect to the completeness of the basis set at the aug'-cc-pVDZ level; using larger basis sets can in fact *reduce* the accuracy of the MP2 method relative to QCISD(T)/CBS for intermediate-sized basis sets. (However, MP2/CBS agrees well with QCISD(T)/CBS for these systems.)

It is encouraging that the MP2/aug'-cc-pVDZ method works well for a variety of baths. MP2 has significant advantages over less rigorous methods such as the Hartree–Fock method and semiempirical methods, because it includes dynamical correlation, which is important for describing long-range forces. Semiempirical methods (AM1, PM3, etc.) are not suitable for describing dispersion interactions and were not considered for the full dimensional direct dynamics calculations. In tests not described in detail here, the MP2/aug'-cc-pVDZ method was found to perform significantly better than double- ζ basis set calculations using HF and several DFT methods, including DFT methods specifically designed for describing dispersion interactions. Furthermore, the MP2/aug'-cc-pVDZ method was found to be reasonably accurate for He interactions with hydrocarbons other than CH₄.

The present strategies may be useful for studying energy transfer in similar systems, but the general accuracy of the MP2/aug'-cc-pVDZ method is unknown. The SAC approach is one method for empirically improving the accuracy of the MP2 method when it is found to be insufficiently accurate. One could also adjust parameters in the basis set or develop custom functionals for use in DFT calculations. None of these strategies is predictive, and employing any of them requires careful comparisons with higher-level interaction energies. To emphasize the difficulty in *predicting* weak van der Waals interactions accurately, we note that the quantitative adjustment made using the SAC approach for H₂ results in a refinement of the well depth of only 30 cm^{-1} , which rivals the mean accuracies of the best empirically adjusted DFT methods designed to model dispersion.³⁷

Separable Approximation to the Potential Energy Surface. While MP2 is an accurate and fairly efficient choice for the systems discussed above, and while we are most interested in computing highly averaged quantities using ensembles of only

several hundreds of trajectories, direct dynamics can nonetheless be computationally prohibitive for many systems of interest. It is therefore desirable to test more efficient methods for describing the potential energy surface for use in larger systems. Direct dynamics calculations using the MP2 and SAC methods discussed above provide benchmark results for validation studies of the approximate potentials discussed next.

The full-dimensional CH₄ + M potential energy surface can be written

$$V(\mathbf{R}) = V_{\text{T}}(\mathbf{R}_{\text{T}}) + V_{\text{M}}(\mathbf{R}_{\text{M}}) + V_{\text{T-M}}(\mathbf{R}) \quad (21)$$

where V_{T} is the intramolecular potential energy surface of the target (CH₄) and is a function of the internal coordinates of CH₄ (\mathbf{R}_{T}), V_{M} is the internal potential energy for the bath gas ($V_{\text{M}} = 0$ for atomic baths) and is a function of the internal coordinates, if any, of the bath (\mathbf{R}_{M}), and $V_{\text{T-M}}$ is the intermolecular potential and is rigorously a function of all of the internal coordinates of CH₄ + M (\mathbf{R}). Here we test the accuracy of further approximating the interaction potential $V_{\text{T-M}}$ as a sum of pairwise atom–atom interactions, that is,

$$V_{\text{T-M}}(\mathbf{R}) \approx \sum_i V_2(R_i) \quad (22)$$

where i labels pairs of intermolecular atoms, and R_i is their separation. Equation 22 neglects higher order terms (e.g., $V_3(R_i, R_j, R_k)$, etc.) in the interaction potential that are responsible for screening, valence saturation effects, and so on. Two forms for V_2 were considered: the Lennard-Jones (LJ) potential

$$V_2(R_i) = D_a[(R'_a/R_i)^{12} - 2(R'_a/R_i)^6] \quad (23)$$

and a modified Buckingham (exp/6) potential

$$V_2(R_i) = A_a \exp(-R_i/B_a) - C_a^6/(R_i^6 + S_a^6) \quad (24)$$

where the subscript a indicates that the fitted parameters depend on the identities of the atoms in the i^{th} pair (i.e., $a = \text{C-He}$, H-He , etc.). We refer to the approximations in eqs 21 and 22 as the "separable pairwise" approximation to the interaction potential. This approximation (along with either the LJ or exp/6 functional forms for V_2) is almost always employed in trajectory studies of energy transfer. The only exception we are aware of is our own previous study of CH₄ + He.¹⁰ The flexibility and fitting accuracy of the separable pairwise approximation is first discussed by comparing the fitted surfaces with the accurate QCISD(T)/CBS energies. The fitting errors are summarized in Table 2.

For He and Ne, exp/6 parameters for eq 24 were obtained by fitting $V_{\text{T-M}}$ to QCISD(T)/CBS energies along three CH₄–M approaches. Alexander and Troya's³⁸ parametrizations (fit to fp-CCSD(T)/CBS energies) were used for Ar and Kr. The separable pairwise approximation with the exp/6 form for V_2 very accurately describes the QCISD(T)/CBS energies for He (Figure 1b) and for the other the atomic baths, with well depth errors of only $1\text{--}8 \text{ cm}^{-1}$ (4–7%) and repulsive wall distance errors of $0.03\text{--}0.04 \text{ \AA}$.

The LJ separable pairwise approach (eq 23) was considered for He, with parameters obtained by fitting to the QCISD(T)/CBS results. This fit is labeled LJ-A and is shown in Figure 1c. A Lennard-Jones interaction potential based on tabulated³⁹ parameters (labeled LJ-B) was also considered; this parametrization is shown in Figure 1d. The LJ-A fit is fairly accurate in the region of the van der Waals well ($\epsilon_{\min} = 1.8 \text{ cm}^{-1}$) but is unable to

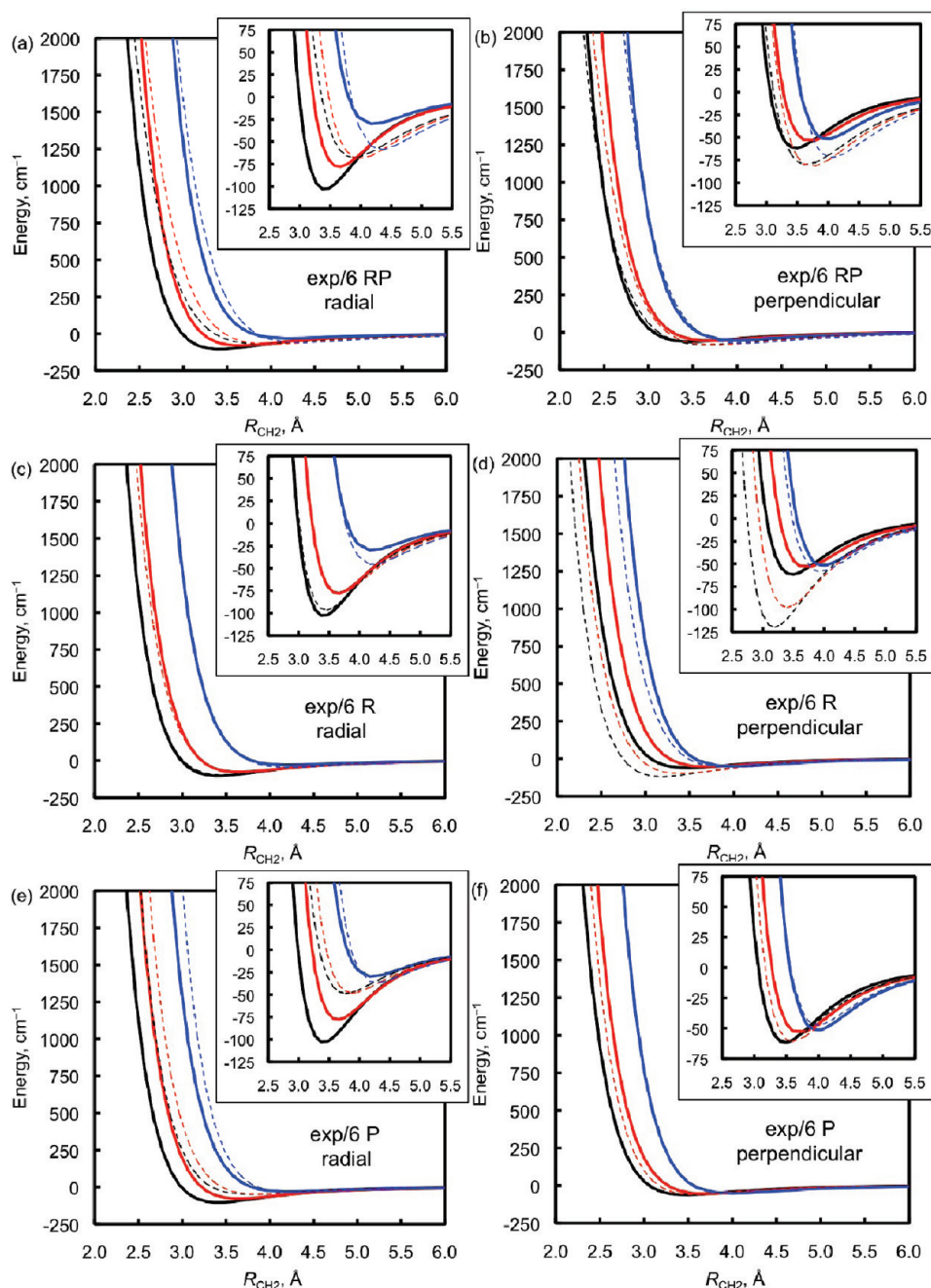


Figure 2. $\text{CH}_4 + \text{H}_2$ interaction potential for the QCISD(T)/CBS (solid) and exp/6 (dashed) methods. The color code for the approaches is the same as in Figure 1. H_2 is aligned in the direction of the approach (radially in (a,c,e) and perpendicularly in (b,d,f). Three exp/6 fits are shown: (a,b) the compromise (RP) fit, (c,d) the radial-only (R) fit, and (e,f) the perpendicular-only (P) fit.

accurately describe the shape of the repulsive wall, leading to large errors in the repulsive wall distances at interaction energies of 2000 cm^{-1} ($\epsilon_{\text{rep}} = 0.3 \text{ \AA}$). The Lennard-Jones fit based on the tabulated parameters somewhat less poorly fits the range of the repulsive walls ($\epsilon_{\text{rep}} = 0.1 \text{ \AA}$) but overpredicts the depths of the van der Waals wells ($\epsilon_{\text{min}} = 7.0 \text{ cm}^{-1}$). The LJ form for V_2 is clearly less accurate than the exp/6 form, and eq 23 was not considered for the other baths.

Next, we consider the flexibility of the exp/6 separable pairwise approach for the diatomic baths. As discussed above, six cuts through the $\text{CH}_4\text{--M}$ interaction potential were

considered for H_2 , three radial approaches and three perpendicular approaches. The exp/6 separable pairwise model was found to be unable to describe the orientation dependence of H_2 accurately, as shown in Figure 2. Three parametrizations of the exp/6 model were therefore obtained: a compromise fit to both the perpendicular and radial data (PR), a fit to the radial data only (R), and a fit to the perpendicular data only (P). In the compromise fit (Figure 2a,b), the well depth is accurately described only on average, and the fit fails to prefer radial orientations. The repulsive wall distances are somewhat shorter-ranged than the QCISD(T)/CBS energies for the radial

Table 3. Frequencies ω and Rotational Constants B for CH₄ (cm⁻¹)

	ω				B
experimental ^a	3019	2917	1534	1306	5.24
MP2 ^b	3209	3065	1565	1344	5.19
SAC ^b	3194	3042	1545	1321	5.19
TB	3252	3162	1690	1570	5.24

^a Ref 30. ^b The aug'-cc-pVDZ basis set was used for the MP2 and SAC calculations.

approaches, as well. Good accuracy was obtained when fitting only one set of approaches (as in the R or P fits), but the resulting fits performed poorly for the set of approaches not included in the fitting data (cf., Figures 2c–f), with well depth errors of 50–75 cm⁻¹. As shown in Table 2, all three fits have similarly large errors averaged over all six approaches, with errors 2–6 times larger than those for the SAC direct dynamics potential discussed above. Nonpairwise corrections to eq 22 to more accurately describe the orientation dependence were not pursued here.

Poor performance of the exp/6 separable pairwise approach was also obtained for the N₂ and CO baths. The N₂ and CO baths both feature prereactive complexes that appear as relatively deep wells in radial approaches to a vertex (i.e., directly to an H atom) of CH₄. (The associated abstraction reaction channels, for example, CH₄ + CO → CH₃ + HCO, are not open at the energies considered here.) These features further degraded the accuracy of the separable pairwise strategy for N₂ and CO, with well depth errors of as much as 100 cm⁻¹ for some approaches. Again, three fits for N₂ were obtained: a compromise (RP) fit, a radial-data-only (R) fit, and a perpendicular-data-only (P) fit. The errors for the three fits are summarized in Table 2, where the average relative error in the well depths and the average error in the repulsive wall distances are shown to be somewhat smaller than for H₂. For CO, two sets of radial approaches were considered to evaluate the approximate potential energy surfaces, with either the C or the O atom on CO oriented toward CH₄, for a total of nine approaches. The exp/6 fits for CO were found to be especially poor, as shown in Table 2, with very large errors in the repulsive wall distances ($\epsilon_{\text{rep}} = 0.1\text{--}0.4$ Å) and large relative errors in the well depths of 20–40%.

The fitted parameters for V_{T-M} for the atomic and diatomic baths are provided as Supporting Information. A separable pairwise fit for M = CH₄ was not pursued.

For H₂, V_M was fit to the calculated curve of Kołos and Wolniewicz.⁴⁰ For N₂, V_M was fit to full valence MRCI+Q/CBS calculations; the calculated curve agrees well with the curve reported by Le Roy et al.⁴¹ For CO, V_M was fit to RKR data⁴² and the experimental dissociation energy.³⁰

We considered two methods for calculating V_T , the intramolecular potential of CH₄: MP2/aug'-cc-pVDZ and the semiempirical extended Hückel⁴³ or tight binding⁴⁴ (TB) model for hydrocarbons of Wang and Mak.^{45,46} The TB model features a minimal orbital description of only 4 orbitals for C and 1 for H, parametrized matrix elements for the molecular Hamiltonian, parametrized core–core repulsion, and a single (i.e., non-iterative) 8 × 8 matrix diagonalization for each gradient evaluation. The TB calculations are several orders of magnitude faster than the MP2/aug'-cc-pVDZ calculations. The vibrational frequencies and rotational constants for CH₄ predicted by the TB, MP2, and SAC methods are compared with experimental values

in Table 3. Agreement with the experimental values is generally good, although the TB method overpredicts the vibrational frequencies.

When trajectory results calculated using the separable pairwise strategy are presented, the results will be labeled “A+B,” where A is the method used to calculate V_T and B is the method used to calculate V_{T-M} ; for example, MP2+exp/6 indicates that MP2 was used to describe the CH₄ potential and eq 24 was used to describe the bath gas interaction. The label “MP2” by itself indicates a nonseparable, full-dimensional direct dynamics calculation using the MP2/aug'-cc-pVDZ method (or, for M = H₂, the SAC variant discussed above).

Initial Conditions for Single Temperature Ensembles. Energy transfer was studied using ensembles of typically 500–5000 trajectories prepared at fixed bath gas temperatures T from 300–4000 K. A scheme for preparing ensembles of CH₄ + He collisions appropriate for calculating energy transfer parameters relevant to the ME energy transfer models discussed above has been described previously.¹⁰ Briefly, trajectories were prepared with a thermal distribution of the initial collision energy E'_c and for fixed initial rotational states J' . The initial vibrational energy E'_{vib} was chosen to be a function of J' and close to the rotationally adiabatic dissociation threshold E_J , with the initial geometries and momenta determined microcanonically. Four modifications were made for the present study.

First, the strategy was generalized to handle molecular baths. The initial internal coordinates and vibrational and rotational momenta of the molecular bath were selected randomly and evenly in time from separate equilibration runs carried out for the isolated molecular bath gas using an Andersen thermostat⁴⁷ set to T . For the diatomic baths, a more rigorous approach of selecting the initial vibrational and rotational states from independent, thermal, quantum mechanical distributions was also tested. These two sampling schemes (which may be called “classical” and “quasiclassical,” respectively) gave energy transfer results within the reported statistical uncertainties, and results obtained using classical sampling are presented here.

Second, the impact parameter b was sampled evenly from $0\text{--}b_{\text{max}}$ whereas in the previous study b^2 was sampled evenly from $0\text{--}b_{\text{max}}^2$. The new scheme intentionally artificially oversampled small b , and this bias was corrected when calculating energy distribution moments, as discussed below and elsewhere.⁴⁸ This scheme was motivated by the observation that large impact parameter trajectories, which are sampled most often in the unbiased sampling procedure, tend to contribute less to the overall energy transfer averages than small impact parameter collisions.

Third, the initial rotational state of CH₄, J' , was sampled from a thermal distribution at T . In the previous work, ensembles of trajectories were prepared with fixed values of J' , and the resulting J' -dependent energy transfer averages were subsequently averaged over J' .

Fourth, the initial vibrational energy E'_{vib} of CH₄ was set to

$$E'_{\text{vib}}(J') = 0.95E_J \quad (25)$$

where E_J is the threshold vibrational energy for rotationally adiabatic dissociation for CH₄, and the rotational thresholds were determined for $K = 0$. Previously, the initial vibrational energy was set to 95% of the average of the rotational thresholds for $K = 0$ and $K = J$. This change corresponds to a very small difference in the initial energy and has a negligible effect on the predicted

energy transfer averages. As discussed previously,¹⁰ E_f varies only weakly with J' and the neglect of the rotational dependence in eq 25 would not introduce significant error for the present calculations for CH₄.

Final State Analyses. The final CH₄ + M separation was chosen to be suitably large (6–8 Å) so that the final internal energy, E , and final total angular momentum, J , of CH₄ could be calculated unambiguously. With the change in the internal energy of CH₄ given by $\Delta E = E - E'$, the ensemble-averaged energy transfer moments were calculated as follows

$$\langle \Delta E \rangle = \frac{Z_{\text{HS}}}{Z_{\text{LJ}}} \sum_{i=1}^N w_i^b \Delta E_i / N \quad (26)$$

$$\langle \Delta E^2 \rangle^{1/2} = \sqrt{\frac{Z_{\text{HS}}}{Z_{\text{LJ}}} \sum_{i=1}^N w_i^b \Delta E_i^2 / N} \quad (27)$$

$$\langle \Delta E_d \rangle = -\frac{Z_{\text{HS}}}{Z_{\text{LJ}}} \sum_{i=1}^N w_i^b \min(\Delta E_i, 0) / N_d \quad (28)$$

where Z_{HS} and Z_{LJ} are the hard sphere and Lennard-Jones collision frequencies (calculated using the parameters in Table 1 and the usual combining rules), respectively, N is the size of the ensemble, and N_d is the number of deactivating collisions. The weights

$$w_i^b = \frac{b_i}{\langle b \rangle} = \frac{2b_i}{b_{\text{max}}} \quad (29)$$

correct for the artificial sampling of the impact parameter b , as discussed above. One-sigma uncertainties are reported for the average energy transfer parameters, as estimated using the bootstrap resampling method.^{49,50}

The per-collision averages in eqs 26–29 are scaled to the Lennard-Jones collision rates Z_{LJ} . We also consider first order average energy transfer rates (i.e., per-time averages), defined

$$\langle r \rangle \equiv Z_{\text{LJ}} \langle \Delta E \rangle n_{\text{M}} \quad (30)$$

$$\langle r_d \rangle \equiv Z_{\text{LJ}} \langle \Delta E_d \rangle n_{\text{M}} \quad (31)$$

$$\langle r^2 \rangle^{1/2} \equiv Z_{\text{LJ}} \langle \Delta E^2 \rangle^{1/2} n_{\text{M}} \quad (32)$$

These quantities have the units of energy transferred per unit time, which we will express as cm^{−1}/s. The average energy transfer rates in eqs 30–32 are independent of the choice for the Lennard-Jones collision frequency. Note that the bath gas concentration n_{M} is related to the temperature T and pressure p via the ideal gas law, $n_{\text{M}} = p/k_{\text{B}}T$, and Z_{LJ} is a function of T ; the averages of ΔE (eqs 26–28) therefore depend differently on temperature than the average rates r (eqs 30–32). The present trajectory approach is closely related to that of Lim and Gilbert,⁵¹ who recognized that, by considering highly averaged quantities, small ensembles of trajectories could be useful in parametrizing energy transfer models in master equation calculations. Furthermore, they pointed out the usefulness of considering energy transfer rates (eqs 30–32) instead of the more commonly considered per-collision energy transfer averages (eqs 26–28).

Zero point energy maintenance was not enforced in the trajectory calculations reported here. Significant numbers of trajectories finished with vibrational energies below those

required by quantum mechanics, including approximately half of trajectories involving diatomic baths. Many remedies for this ubiquitous problem have been proposed, but none is wholly satisfactory. Furthermore, we note that in the present context, it may be preferable to use a consistently classical picture rather than a semiclassical one. For example, if we consider the ensemble-averaged energy transferred in collisions involving two species that are both initially equilibrated to the same temperature, we would expect to calculate $\langle \Delta E \rangle = 0$. This is precisely what would be obtained using a consistently classical picture such as the one used here. On the other hand, if one fragment featured frequent zero point energy violations, throwing out these trajectories or correcting them in some way would in general result in incorrect, nonzero values of $\langle \Delta E \rangle$. Of course, in some contexts, enforcing zero point energy is crucial to obtaining useful information, and the mapping of the quantum mechanical concept of zero point energy maintenance (and, more generally, quantized vibrations) onto classical mechanics remains an important area of continued study. For the highly averaged energy transfer moments considered here, however, a consistent classical treatment is a reasonable and likely accurate approach.

Multitemperature Ensembles. The single temperature ensembles described above consist of trajectories with thermal distributions of J' and E'_c for some bath gas temperature T . The same ensemble of trajectories could be used to calculate energy transfer averages at a different temperature T_2 by assigning weights to each trajectory based on the relative thermal populations of J' and E'_c at T and T_2 . This idea was generalized here to calculate energy transfer averages over a range of bath gas temperatures using a single ensemble of trajectories as follows.

For each trajectory in a multitemperature ensemble, a sampling temperature, T_s , was selected randomly and evenly from T_{min} to T_{max} . The initial rotational state and relative collision energy were then chosen from appropriate thermal distributions for the sampling temperature T_s . The resulting ensembles were used to calculate energy transfer averages any temperature T by weighting each trajectory by

$$w_i^T = \frac{P_J(T; J'_i) P_c(T; E'_{c,i})}{\int_{T_s=T_{\text{min}}}^{T_s=T_{\text{max}}} dT_s P_J(T_s; J'_i) P_c(T_s; E'_{c,i}) / (T_{\text{max}} - T_{\text{min}})} \quad (33)$$

in eqs 26–28, where P_J and P_c describe thermal distributions of the initial rotational state and relative collision energy, respectively. This scheme does not introduce any additional approximations and may be more useful than sampling at fixed values of T .

Somewhat more complicated distributions of T_s could be used to produce ensembles with energy transfer moments with equal relative statistical uncertainties over the entire temperature range T_{min} to T_{max} . In the current strategy, the relative statistical uncertainties are roughly twice as large at the edges of the temperature range than at intermediate temperatures.

Trajectory calculations were carried out using the freely available direct dynamics trajectory code DiNT⁵² interfaced with the Molpro program package.⁵³ Ensemble sizes were chosen such that the direct dynamics ensembles had relative 1σ uncertainties in $\langle \Delta E_d \rangle$ of $\sim 10\%$ (100–2000 trajectories) and the less expensive TB+exp/6 ensembles had relative 1σ uncertainties in $\langle \Delta E_d \rangle$ of a few percent (5000–20000 trajectories).

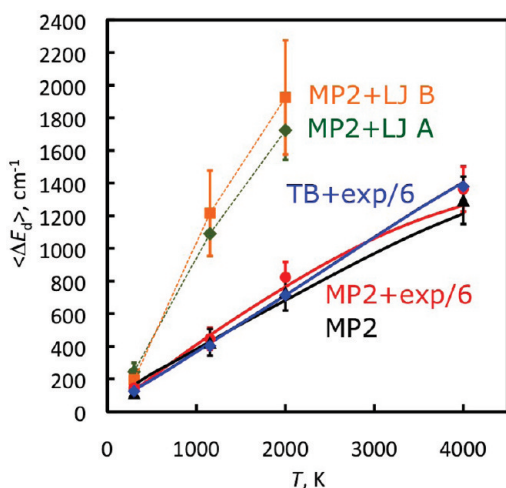


Figure 3. Average downward energy transfer for $M = \text{He}$ for five potential energy surfaces. The symbols are results obtained from single temperature ensembles. The solid lines are results obtained using the multitemperature sampling scheme. The dashed lines connect the LJ results.

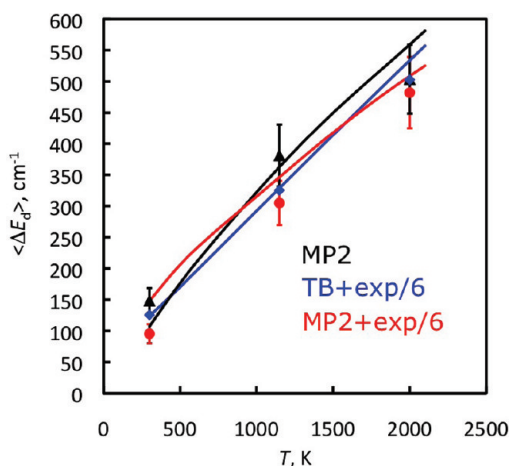


Figure 4. Average downward energy transfer for $M = \text{Ne}$ for several potential energy surfaces. The symbols are results obtained from single temperature ensembles. The solid lines are results obtained using the new multitemperature sampling scheme.

III. RESULTS AND DISCUSSION

III.A. Tests of the Separable Potential Approximation.

Energy transfer averages were previously reported¹⁰ for He using a full dimensional MP2/aug'-cc-pVDZ potential energy surface. These calculations were repeated for the present study to confirm the accuracy of the new sampling procedures; the present MP2 results for $\langle \Delta E_d \rangle$ at 300–2000 K are $\sim 20\%$ higher than the previously published results due to the improved sampling over J' employed here. These differences are small and close to the combined statistical uncertainties in the MP2 calculations in the present and previous studies.

A comparison of the predicted values for $\langle \Delta E_d \rangle$ for $M = \text{He}$ calculated using the full dimensional MP2 method as well as several separable pairwise potential energy surfaces is shown in Figure 3. The Lennard-Jones approximation for the intermolecular potential performs very poorly relative to the MP2 results.

The LJ-A potential, which was parametrized to fit the van der Waals well, overestimates $\langle \Delta E_d \rangle$ by 120–150%. When tabulated values for the Lennard-Jones parameters are used, the LJ-B potential overestimates $\langle \Delta E_d \rangle$ by 70% at 300 K and by almost a factor of 3 at 1150 and 2000 K. As discussed in section II.B, neither Lennard-Jones potential accurately describes the repulsive wall (the LJ interaction is “harder” than the accurate interaction), and this deficiency introduces considerable error into the calculated results. It is likely that these deficiencies in the LJ potential for modeling the repulsive wall are general, and one can conclude that LJ interactions cannot be used for accurate energy transfer studies.

The exp/6 separable pairwise model was tested against the full-dimensional MP2 direct dynamics calculations for two atomic baths (He and Ne), and comparisons of $\langle \Delta E_d \rangle$ calculated using the MP2 and MP2+exp/6 potential energy surfaces are shown in Figures 3 and 4 for He and Ne, respectively. The predicted values of $\langle \Delta E_d \rangle$ obtained using the MP2+exp/6 potential energy surfaces are in excellent agreement with the full dimensional direct dynamics results, differing from one another at 1150 and 2000 K by less than 15%. The relative differences between the MP2 and MP2+exp/6 predictions are larger at 300 K, although the differences ($\sim 30\%$) are close to the estimated 1σ statistical uncertainties. These results suggest that the neglect of many-body terms in eq 22 is not a significant source of error for the atomic baths, so long as accurate repulsive walls, such as those in the fitted exp/6 potential energy surfaces, are used. The good performance of the exp/6 parametrizations is consistent with the small fitting errors of the exp/6 interaction potential, which accurately describes both the depth of the van der Waals well and the shape of the repulsive wall.

For both He and Ne, the predicted energy transfer averages were found to be insensitive to the level of theory used to describe the target potential energy surface V_T , with the MP2+exp/6 and TB+exp/6 values for $\langle \Delta E_d \rangle$ differing by only 5–15%. This result is perhaps surprising; the TB method overpredicts the vibrational frequencies for CH_4 , as shown in Table 3, such that the rotationless harmonic density of states ρ at the dissociation threshold for the TB potential is 40% smaller than that for the MP2 surface (although the differences in the anharmonic state densities of the two methods may be smaller than differences in the harmonic state densities). One may expect energy transfer to be a sensitive function of ρ . We note that in our own unpublished work, we have found that while ρ is a sensitive function of E_{vib} near threshold, $\langle \Delta E_d \rangle$ is not. This, along with the good agreement between the present TB+exp/6 and MP2+exp/6 results, suggests that the dependence of $\langle \Delta E_d \rangle$ on ρ is small for the present systems. Further systematic studies of this issue are beyond the scope of the present work. We simply note that the good accuracy of the TB+exp/6 method is encouraging, as the Wang and Mak TB parametrization predicts fairly accurate structures and frequencies for a variety of hydrocarbons⁴⁵ and is very efficient in the trajectory calculations. Note also that the dependence of the predicted values of $\langle \Delta E_d \rangle$ or other energy transfer moments on ρ is separate from the dependence of unimolecular rate coefficients on ρ . As shown by Troe¹ and in eq 20, low-pressure limit unimolecular rate coefficients are directly proportional to ρ and so errors in ρ lead to proportional errors in k_0 . In the present application, errors in k_0 could also arise due to errors in ρ associated with the potential energy surfaces used in the classical trajectory calculations, via the calculated energy transfer averages. As mentioned above, the

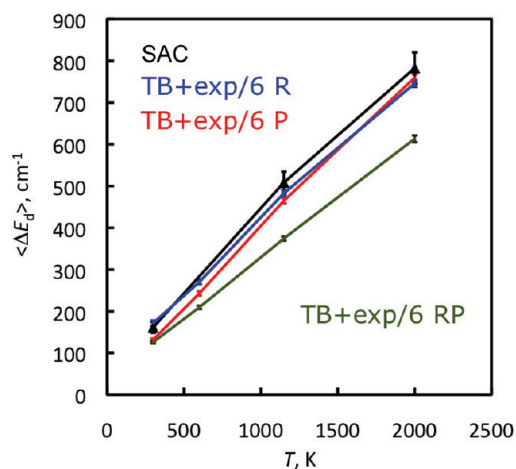


Figure 5. Average downward energy transfer for $M = \text{H}_2$ for four potential energy surfaces.

sensitivity of $\langle \Delta E_d \rangle$ on E_{vib} is small, and one may interpret this to indicate that the sensitivity of $\langle \Delta E_d \rangle$ on ρ is also small. It is therefore not expected to be a significant source of error, and in fact may be preferred, to use different treatments for ρ in the master equation analysis and when running the classical trajectories.

Results obtained using the multitemperature sampling scheme are in excellent agreement with those obtained from the single temperature strategy, as shown in Figures 3 and 4, and the multitemperature scheme provided more precise results for a fixed total number of trajectories. For example, with ensemble sizes of 120, 340, 575, and 1100 $\text{CH}_4 + \text{He}$ trajectories for 300, 1150, 2000, and 4000 K, respectively, the MP2 results have relative 1σ errors of $\sim 15\%$. In contrast, a 2000 trajectory ensemble using the multitemperature strategy predicted results with 1σ errors of only 5–10% over the temperature range 300–4000 K. The improved statistics facilitated the present comparisons of the various potential energy surfaces for the atomic baths.

Next, we compare the TB+exp/6 separable pairwise method with full dimensional SAC calculations for the diatomic bath, H_2 . As discussed above and in contrast to the atomic colliders, the pairwise exp/6 functional form is not flexible enough to describe the orientation dependence interaction potential, and three exp/6 parametrizations (R, P, and RP) were obtained. The values of $\langle \Delta E_d \rangle$ predicted by the three exp/6 fits are compared with the full dimensional SAC results in Figure 5. The compromise fit (exp/6 RP) predicts values of $\langle \Delta E_d \rangle$ that are $\sim 25\%$ lower than the SAC results, whereas the exp/6 R predictions are in good agreement with the SAC results. The exp/6 P fit is accurate at elevated temperatures but performs less well at 300 K. It is difficult to rationalize these results based on the quality of the three exp/6 parametrizations summarized in Table 2; the RP parametrization more accurately fits the range of the repulsive walls than the R and P parametrizations, and all three have similarly poor descriptions of the well depths, on average. We conclude that it is likely that the good agreement of the exp/6 R fit with the SAC results is accidental and that the range of results obtained from the exp/6 fits is representative of an additional uncertainty in the predicted exp/6 results due to the separable pairwise approximation for H_2 .

Although we do not have full dimensional MP2 trajectory results for $M = \text{N}_2$ and CO, we can gain further insight into the

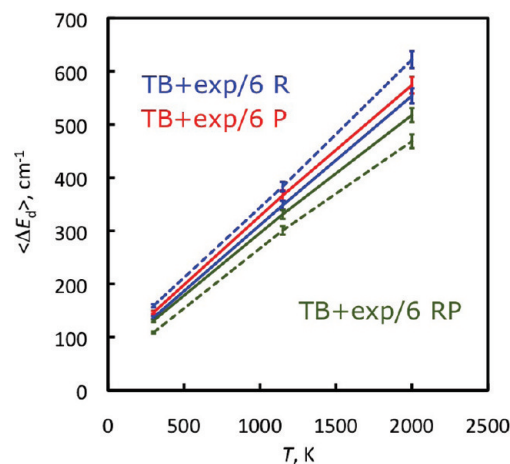


Figure 6. Average downward energy transfer for $M = \text{N}_2$ (solid) and CO (dashed) for several potential energy surfaces. The TB+exp/6 P potential was not tested for CO.

accuracy of the separable pairwise approximation for the diatomic baths by comparing the results of several reasonable exp/6 parametrizations for N_2 and CO. As discussed above, three exp/6 fits for N_2 were obtained. For CO, we consider only the best two exp/6 fits: the compromise (RP) fit and the fit to the radial (R) data with the O atom facing CH_4 . Predicted values of $\langle \Delta E_d \rangle$ for the exp/6 fits for N_2 and CO are shown in Figure 6. The N_2 results differ from one another by only $\sim 10\%$, whereas the CO results differ from each other by 25–50%. Again, the relative magnitudes of these uncertainties in $\langle \Delta E_d \rangle$ do not appear evident from the quality of the fitted potentials for N_2 and CO indicated by the errors shown in Table 2.

The sensitivity of calculated energy-transfer averages to properties of the potential energy surface used in trajectory calculations has been studied previously. In these previous studies, the predicted energy transfer averages were found to be largely insensitive to the potential energy surface used to describe the target and to depend sensitively on the functional form used to describe the interaction potential and, in particular, on the range and “softness” of the repulsive wall.^{12,14,51,54–56} The present results agree with these qualitative conclusions. The full dimensional MP2 and SAC direct dynamics calculations reported here allow us to further quantify the errors associated with the use of approximate potential energy surfaces, at least for $\text{CH}_4 + M$. For the atomic baths, the neglect of nonpairwise terms in the interaction potential introduces a negligible uncertainty into the predicted energy transfer averages so long as parametrized exp/6 pairwise interactions are used. The use of LJ pairwise interactions leads to significant errors and is not appropriate for quantitative or even semiquantitative studies. For the diatomic baths, on the other hand, the exp/6 separable pairwise strategy is not flexible enough to describe the interaction potential accurately. The resulting ambiguities in the fitted parameters introduce an additional uncertainty of up to 50% into the predicted energy transfer averages for the diatomic baths. Unfortunately, the quality of the calculated energy transfer averages is not evident from the quality of the fitted interaction potentials, at least not from the simple errors summarized in Table 2. Finally, we note that additional uncertainties may be expected when applying the separable pairwise strategy to targets that are less spherical than CH_4 , even for atomic baths, as these systems may

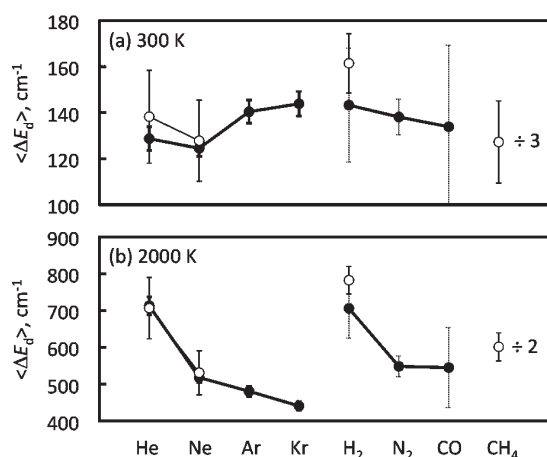


Figure 7. Energy transfer averages scaled to Lennard-Jones collision rates for deactivating collisions in eight baths at (a) 300 and (b) 2000 K for the MP2 (open symbols) and TB+exp/6 (closed symbols) potential energy surfaces. For the diatomic baths, the average of the several TB+exp/6 parametrizations considered is shown. The error bars are 1σ statistical uncertainties, except for the TB+exp/6 results for the diatomic baths where the error bars are the standard deviations of the results for the several TB+exp/6 parametrizations. Note that the CH_4 results are scaled down by a factor of 3 and 2 at 300 and 2000 K, respectively.

have a more complicated interaction potential orientation dependence.

III.B. Comparison of the Baths. Next, a comparison of the relative energy transfer efficiencies of the eight baths is made. The average energy transferred in deactivating collisions $\langle \Delta E_d \rangle$ calculated using the TB+exp/6 method is shown at 300 and 2000 K in Figure 7 for the eight baths. Full dimensional direct dynamics results are also shown, if available. The MP2 and TB+exp/6 potential energy surfaces predict very similar values for $\langle \Delta E_d \rangle$, with magnitudes that agree within the 1σ statistical uncertainties for He and Ne. As discussed above, the TB+exp/6 predictions for the diatomic baths have additional uncertainties of 10–50% due to ambiguities in the fitted surfaces. The diatomic baths have energy transfer averages similar in magnitude to those for the atomic baths, but the additional uncertainties for N_2 and CO preclude a quantitative comparison of their energy transfer efficiencies with the other baths.

At room temperature (Figure 7a), the magnitude of $\langle \Delta E_d \rangle$ is very similar for all the baths except for CH_4 , which transfers nearly three times as much energy, on average, in deactivating collisions. The predicted values for $\langle \Delta E_d \rangle$ are somewhat larger (by only 10–20 cm^{-1}) for H_2 , Ar, and Kr than for He and Ne, with differences close to the statistical uncertainties.

The trend in $\langle \Delta E_d \rangle$ with respect to the bath gas differs at elevated temperatures. At 2000 K (Figure 7b), He and H_2 are significantly stronger colliders than the other atomic and diatomic baths, transferring $\sim 40\%$ more energy on average per deactivating collision. He and H_2 transfer similar amounts of energy as one another, and, again, CH_4 is the strongest collider. The trajectory results indicate that the change in the relative energy transfer efficiencies occurs around 500 K, suggesting that room temperature relative efficiencies may not be useful predictors of relative efficiencies at combustion temperatures.

The results in Figure 7 are scaled to Lennard-Jones collision frequencies, that is, $\langle \Delta E_d \rangle$ is the average energy transferred per

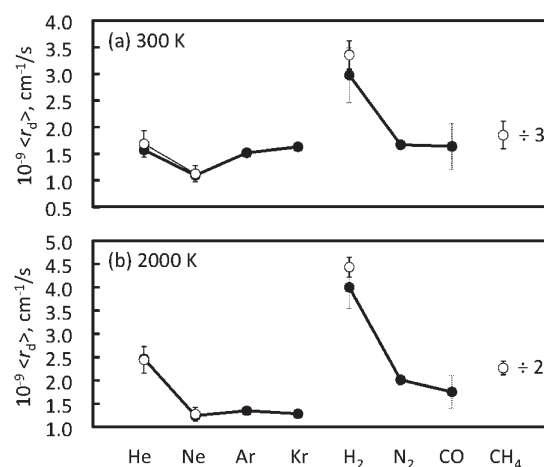


Figure 8. Energy transfer rate coefficients for deactivating collisions in eight baths at (a) 300 and (b) 2000 K and 1 Torr for the MP2 (open symbols) and TB+exp/6 (closed symbols) potential energy surfaces. For the diatomic baths, the average of the several TB+exp/6 parametrizations considered is shown. The error bars are 1σ statistical uncertainties, except for the TB+exp/6 results for the diatomic baths where the error bars are the standard deviations of the results for the several TB+exp/6 parametrizations. Note that the CH_4 results are scaled down by a factor of 3 and 2 at 300 and 2000 K, respectively.

deactivating collision, assuming collisions are occurring at the Lennard-Jones collision rate. This choice, although conventional, is arbitrary. Furthermore, the accuracy of any particular set of the Lennard-Jones parameters and of the usual Lennard-Jones combining rules is unknown in the present context, and different choices for the collision rate will, in general, introduce different temperature dependences in $\langle \Delta E_d \rangle$. Figure 8 presents the same data as Figure 7 but without scaling to Lennard-Jones collision frequencies, that is, $\langle r_d \rangle$ is defined by eq 30 as the average first order energy transfer rate coefficient for deactivating collisions. At room temperature, Figure 8 shows H_2 to be an especially efficient collider, with $\langle r_d \rangle$ more than twice as large for H_2 than for the atomic baths. Ne is a relatively poor collider, with the other atomic baths differing from one another by less than 10% in $\langle r_d \rangle$. At 2000 K, He is twice as efficient as Ne, Ar, and Kr, with H_2 again more efficient than the atomic baths. The predicted value for $\langle r_d \rangle$ for CH_4 is 70% larger than H_2 at 300 K, but the two baths predict similar values of $\langle r_d \rangle$ at 2000 K.

Overall, the trends in $\langle \Delta E_d \rangle$ and $\langle r_d \rangle$ are similar, but $\langle r_d \rangle$ may be expected to more clearly predict the quantitative kinetic effect of the different baths in promoting dissociation. The usefulness of considering the average energy transfer rate coefficients (in contrast to the per-collision energy transfer averages) has been emphasized by Lim and Gilbert.^{23,51}

The relative collisional energy transfer efficiencies of typical bath gases are of considerable interest, though few systematic experimental or theoretical studies exist. As noted in the Introduction and discussed in detail by Gilbert,²³ in one set of trajectory studies for rare gas collisions with azulene at 300 K He was predicted to be the most efficient atomic collider in contrast to experimental results for the same system.²⁶ Good agreement between the experimental and theoretical results was obtained for the heavier atomic baths. Gilbert suggested that more accurate potential energy surfaces were needed for He. The present results for rare gas collisions with CH_4 , using the interaction potential energy surfaces validated in section III.A,

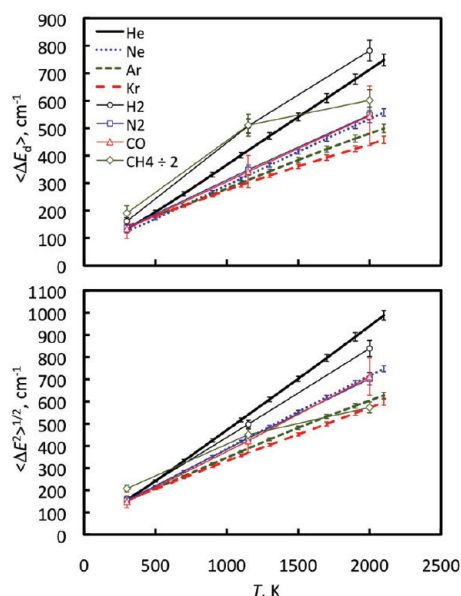


Figure 9. (a) Average energy transferred in deactivating collisions and (b) the root-mean-squared energy transferred for eight baths. The CH₄ results are scaled down by a factor of 2.

Table 4. Predicted Energy Transfer Parameters for eq 1^a

	$\alpha_{300}, \text{cm}^{-1}$	n
He	117	0.95
Ne	104	0.86
Ar	115	0.75
Kr	123	0.67
H ₂	162	0.83
N ₂	130	0.76
CO	130	0.76
CH ₄	390	0.60

^a The resulting values of $\alpha(T)$ may be assigned 1σ uncertainties of 15% arising from statistical uncertainties and from limitations in the assumed functional form of eq 1. The use of the separable pairwise approach for the diatomic baths introduces additional uncertainties of 20–40% for these baths. See text for details.

predict He to be slightly less efficient than the other atomic baths at room temperature, which may support Gilbert's analysis. Rabinovitch and co-workers⁵⁷ experimentally studied the isomerization of methyl isocyanide near room temperature in 19 baths, and, in another set of systematic experimental studies, Michael and co-workers measured a series of low pressure rate coefficients for NO₂, HO₂, HNO, HCO, and C₂H₅ recombination reactions in several baths.^{27,58–60} In general, these studies found He, Ar, and Kr to have efficiencies similar to one another, Ne to be less efficient than the other atomic baths, and H₂ to be more efficient. The relative energy transfer efficiency of He was also shown by Michael et al.⁶⁰ to increase with temperature for NO₂ recombination at 200–500 K. These experimental trends are consistent with the present work. For N₂, however, the experimental work generally found rate coefficients somewhat larger than those for He, whereas in the present work the heavier diatomic baths have efficiencies similar to the heavier atomic baths. This discrepancy could indicate further uncertainties in the present trajectory calculations for diatomic baths due to the

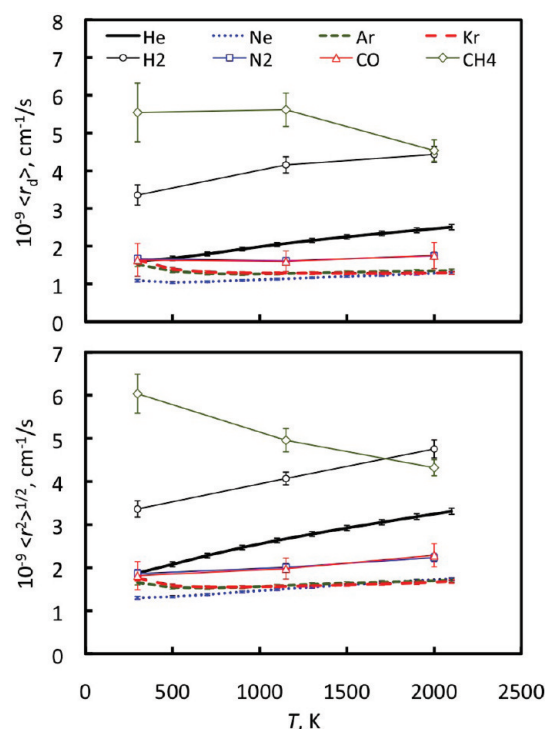


Figure 10. (a) Average energy transfer rate coefficient in deactivating collisions and (b) root-mean-squared energy transfer rate coefficient at 1 Torr for eight baths.

separable pairwise approximation for the interaction potential, as discussed above. Finally, we note again the temperature dependence in the relative collisional energy transfer averages shown in Figure 7 may complicate attempts at generalizations about relative bath gas efficiencies obtained over limited temperature ranges.

Figure 9 summarizes $\langle \Delta E_d \rangle$ and $\langle \Delta E^2 \rangle^{1/2}$ for M = He, Ne, Ar, and Kr (TB+exp/6), H₂ (SAC), CH₄ (MP2), and N₂ and CO (averaged over the several TB+exp/6 parametrizations). The relative bath gas efficiencies were discussed above, and here we focus on the temperature dependence of the predicted energy transfer averages. The data for $\langle \Delta E_d \rangle$ were fit to the empirical formula in eq 1; both α_{300} and n were treated as adjustable parameters and were determined by minimizing the mean unsigned error to the data in Figure 9. For the atomic baths, $\alpha_{300} = 104\text{--}123 \text{ cm}^{-1}$ and $n = 0.67\text{--}0.95$, as shown in Table 4. These values are consistent with typical empirical determinations of α_{300} and n , where $\alpha_{300} = 50\text{--}300 \text{ cm}^{-1}$ and $n \approx 1$.

The present data suggest a more complicated temperature dependence than is assumed in eq 1. The best fit parameters to eq 1 for the temperature range 300–2000 K underpredicted the calculated room temperature values of $\langle \Delta E_d \rangle$ by 10–20% for the atomic baths. For the polyatomic baths, eq 1 was again unable to accurately describe the entire temperature range considered, and the optimized parameters summarized in Table 4 overpredicted the 1150 K data by as much as 15%. This more complicated temperature dependence than what is often assumed (as in eq 1) may contribute to the general difficulty in developing an intuition about how the parameters α_{300} and n depend on the bath gas and target.

The predicted values for $\langle \Delta E^2 \rangle^{1/2}$ (Figure 9b) show a stronger temperature dependence than $\langle \Delta E_d \rangle$. The relative ordering of

the predicted values of $\langle\Delta E^2\rangle^{1/2}$ for the eight baths at 300 and 2000 K is similar to that for $\langle\Delta E_d\rangle$. Specifically, at 300 K, the values for $\langle\Delta E^2\rangle^{1/2}$ for the atomic baths, N₂, and CO are similar (148–155 cm^{−1}), with $\langle\Delta E^2\rangle^{1/2}$ only slightly larger for H₂ (162 cm^{−1}) and much larger for CH₄ (416 cm^{−1}). At 2000 K, the predicted values for the root-mean-squared energy transfer for He and H₂ (940 and 839 cm^{−1}) are larger than those for the other atomic ($\langle\Delta E^2\rangle^{1/2}$ = 716, 604, and 572 cm^{−1} for Ne, Ar, and Kr) and diatomic baths ($\langle\Delta E^2\rangle^{1/2}$ = 702 and 712 cm^{−1} for N₂ and CO). Again, CH₄ is the strongest collider with $\langle\Delta E^2\rangle^{1/2}$ = 1146 cm^{−1} at 2000 K.

The average energy transferred in all collisions $\langle\Delta E\rangle$ is negative or very close to zero for 300–2000 K, with similar magnitudes for all the baths except He, H₂, and CH₄; for these baths, $\langle\Delta E\rangle$ is somewhat more negative. The magnitude of $\langle\Delta E\rangle$ is small (only tens of cm^{−1}) and is typically close to or smaller than the statistical uncertainties for the ensembles considered here. Significantly more trajectories would be required to calculate $\langle\Delta E\rangle$ accurately enough to be used in collision models. We note that the average initial vibrational energy $\langle E'_{\text{vib}}\rangle \approx 4.5$ eV corresponds to an initial vibrational temperature of ~ 6000 K ($T_{\text{vib}} = \langle E'_{\text{vib}}\rangle/k_{\text{B}}N_{\text{vib}}$, with $N_{\text{vib}} = 9$). The initial rotational distribution for our ensembles is already in thermal equilibrium with the bath. The net energy transferred is therefore negative as the bath and the rotational degrees of freedom equilibrate the vibrational degrees of freedom, that is, as the vibrational degrees of freedom cool. The small values of ΔE reflect the “weak” nature of these collisions, that is, many collisions would be required to bring the vibrational energy into equilibrium with the bath.

Figure 10 presents $\langle r_d \rangle$ and $\langle r^2 \rangle^{1/2}$ for the same trajectory ensembles shown in Figure 9. The trends in the energy transfer rates with respect to the bath gases shown in Figure 10 are somewhat different than the trends in the per-collision averages shown in Figure 9. First, $\langle r_d \rangle$ and $\langle r^2 \rangle^{1/2}$ are both inversely proportional to the reduced mass of the system (roughly proportional to $\mu^{-1/2}$ if μ is the CH₄–M reduced mass) for the series of atomic baths and for the series of diatomic baths. This dependence arises primarily due to the dependence of the collision frequency on the relative mass, which is not included in Figure 9. Second, for systems with especially shallow van der Waals wells (He and H₂), the temperature dependence is positive, whereas the baths with relatively deep van der Waals wells show an increased relative importance at room temperature, leading to weak or negative temperature dependences. Third, the diatomic baths N₂ and CO are somewhat more efficient than the heavy atomic baths, despite having similar reduced masses and well depths. The energy transfer rate for CH₄ is even larger than the energy transfer for the diatomic baths, again despite having a similar well depth and a smaller reduced mass. This likely reflects the enhancement of energy transfer as the number of vibrational and rotational modes in the bath gas increases. Figures 9 and 10 present the same data, but the simple trends identified here (those respect to the relative mass, the well depth, and the dimensionality of the bath gas) are more apparent in the energy transfer rates shown in Figure 10.

III.C. Decomposition Rate Coefficients and a Comparison with Experimental Rate Coefficients for M = He, Ar, Kr, and CH₄. Decomposition rate coefficients were calculated using eq 1, the parameters summarized in Table 4 obtained from the trajectory ensembles described in section III.B, and the ME approach discussed in section II. Low pressure limiting rate coefficients k_0 near 2000 K and pressure dependent rate

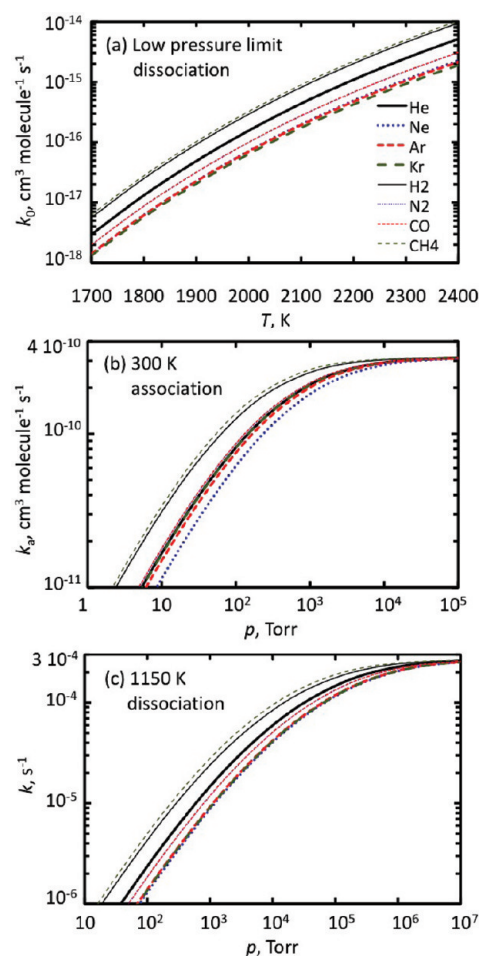


Figure 11. Comparison of the (a) low pressure limit dissociation rate coefficient, (b) association rate coefficient at 300 K, and (c) dissociation rate coefficient at 1150 K for CH₄ in eight baths.

coefficients k at 300 and 1150 K are shown for eight baths in Figure 11. The values for k_0 at 2000 K (Figure 11a) differ by as much as a factor of 5, ranging from $0.3\text{--}1.6 \times 10^{-4}$ cm³ molecule^{−1} s^{−1}. The differences in the decomposition rate coefficients due to the bath gases, of course, decrease as the rate coefficients approach the high pressure limit, as shown in the falloff rate coefficients in Figure 11b,c. As suggested by Figures 7 and 8, the relative efficiencies of the bath gases change as a function of temperature; this is evident in the different ordering of the association and dissociation rate coefficients with respect to the bath gas at 300 and 1150 K in Figure 11b and c, respectively. The trends in the effect of the eight baths on k are well reproduced by the trends in the average energy transfer rate coefficients shown in Figure 10; these trends are more closely related to the trends in the average energy transfer rates than the per-collision energy transfer averages shown in Figure 9, as suggested by eq 20 and elsewhere.^{23,51} We emphasize that the energy transfer rate coefficients can be obtained just as easily from the trajectory calculations as the energy transfer averages.

Next, the present decomposition rate coefficients for M = He, Ar, Kr, and CH₄ are compared with available experimental results. In Figure 12a, the predicted results for k_0 in Ar are compared with experimental values from several groups^{61–65} and with the recommended value of Baulch et al.⁶⁶ The present

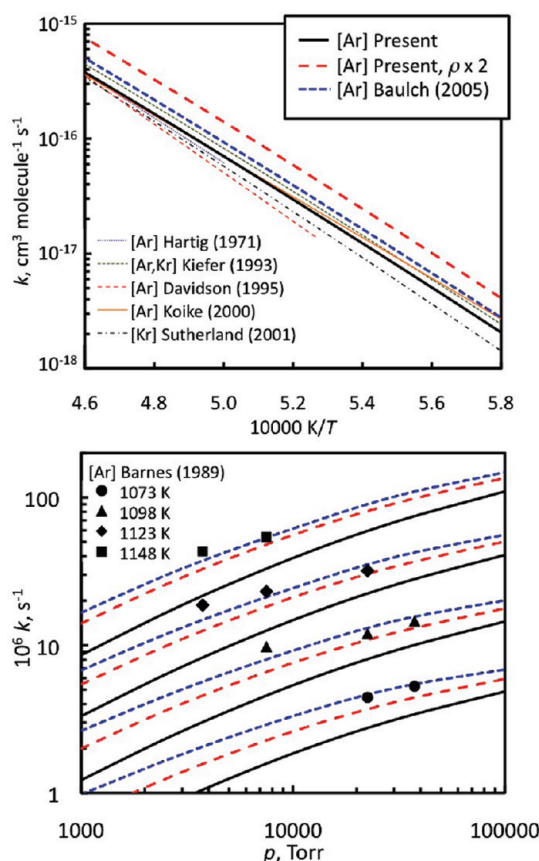


Figure 12. Present predicted (a) low pressure and (b) falloff decomposition rate coefficients for CH_4 in Ar (black solid lines) compared with several experimental results in Ar and Kr (thin lines in (a) and symbols in (b)) and with the recommended value of Baulch et al. (blue dotted lines). The effect on the present prediction of scaling the vibrational frequencies to increase the density of states of CH_4 at threshold by a factor of 2 is shown as dashed red lines.

prediction for Ar is $\sim 25\%$ lower than the recommended value, which was based largely on the measured rate coefficients of Kiefer and Kumaran⁶³ and agrees well with Hartig et al.⁶¹ and Koike et al.⁶⁴ The most recent measurement (Sutherland et al.⁶⁵ in Kr) and the revised measurement from Davidson et al.⁶² are somewhat lower and are in better agreement with the predicted results. Overall, the agreement between the predicted and measured values for k_0 in Ar is excellent.

In Figure 12b, the present predicted values of k in Ar near 1100 K are compared with the experimental falloff results of Barnes et al.⁶⁷ and with the recommended values of Baulch et al.⁶⁶ The predicted values of k are again lower than the measured and recommended rate coefficients, with the differences as large as a factor of 2. The present theoretical predictions underestimate both the low pressure and falloff experimental rate coefficients. As discussed by Troe,¹ the low-pressure limit rate coefficient is approximately proportional to the density of states at threshold, and anharmonic vibrational corrections to the RRHO density of states would tend to increase the density and therefore the rate coefficient. Nguyen and Barker⁶⁸ calculated an anharmonic correction to the density of states for several systems including CH_4 . At threshold for dissociation, this correction is close to a factor of 2, in agreement with empirical corrections calculated and tabulated by Schmatz.⁶⁹ We approximated such an

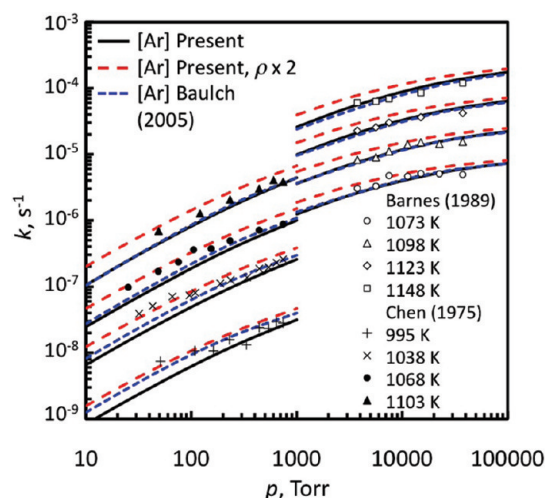


Figure 13. Predicted falloff rate coefficients for CH_4 decomposition in CH_4 (black lines). Several experimental results (symbols) and the recommended values of Baulch et al. (blue dotted lines) are also shown. The effect on the present prediction of increasing the density of states of CH_4 at threshold by a factor of 2 is shown as dashed red lines.

anharmonic correction to the density of states for CH_4 by scaling all of the harmonic frequencies by 0.91. This scaling doubled the rotationless harmonic density of states at the dissociation threshold. The equilibrium constant and partition functions were not scaled, such that the high pressure limiting rate coefficients were not affected. As seen in Figure 12a, the low pressure rate coefficient is doubled when the threshold density of states is doubled, consistent with Troe's analysis. The resulting values of k_0 obtained, however, overestimate the recommended values of k_0 by $\sim 50\%$ and are in worse agreement with experiment than the harmonic calculation. On the other hand, including the effect of anharmonicity significantly improves the agreement of the predicted results with the experimental falloff rate coefficients in Figure 12b, although the predicted rates are still somewhat too low.

In Figure 13, falloff rate coefficients for $\text{CH}_4 (+ \text{CH}_4) \rightleftharpoons \text{CH}_3 + \text{H} (+ \text{CH}_4)$ are compared with the measured rate coefficients of Barnes et al.⁶⁷ and Chen et al.⁷⁰ and with the recommended values of Baulch et al.⁶⁶ The predicted values are in good agreement with the measured rate coefficients and, on average, somewhat underpredict the measured values. Approximately correcting for the vibrational anharmonicity of CH_4 increases the predicted decomposition rate coefficients by up to a factor of 2, but in this case it is unclear whether or not this adjustment systematically improves the agreement with the experimental results. In fact, the adjustment is close to the recommended uncertainty of Baulch et al.⁶⁶ ($\Delta \ln k_0 = \pm 0.3$).

We previously showed¹⁰ that using direct dynamics trajectory ensembles to predict α for $\text{M} = \text{He}$ and RRHO estimates for the CH_4 density of states resulted in association and decomposition rate coefficients for CH_4 that were in close agreement with experimental results.^{67,71} A similar comparison is made in Figure 14, where the newly predicted values for α for He are used. As indicated above, the present values for α are in good agreement with those from the previous study, and the resulting rate coefficients are again in good agreement with the experimental rate coefficients and with the recommended values of Baulch et al.⁶⁶ Scaling the frequencies to double the density of

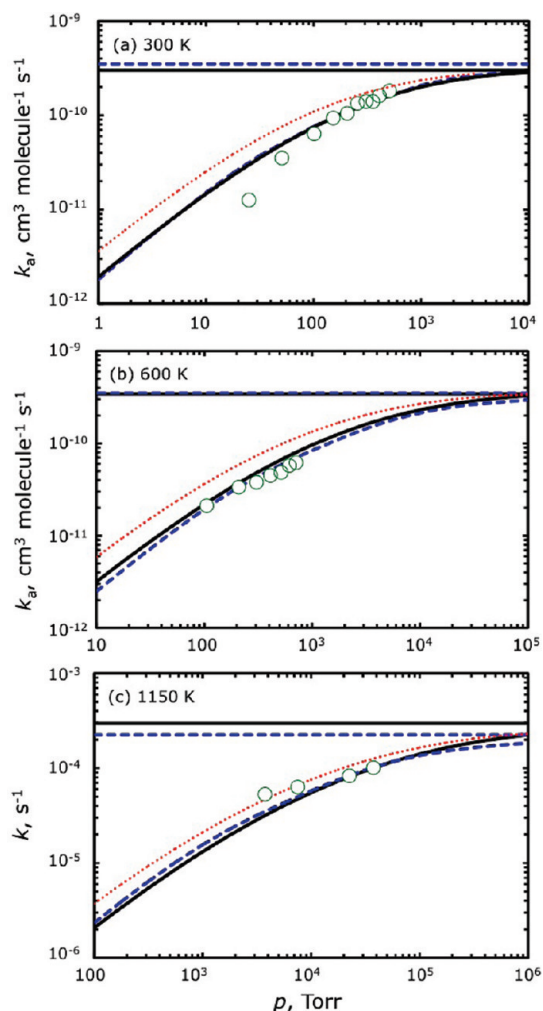


Figure 14. Association (k_a) and dissociation (k) rate coefficients for CH_4 in He at (a) 300, (b) 600, and (c) 1150 K. The present predicted values (black solid lines) are compared with the recommended values of Baulch et al. (blue dashed lines) and experimental values from two groups^{67,71} (circles). The red dotted lines show the effect on the present predicted values of artificially doubling the density of states of CH_4 at threshold. The horizontal lines show the high pressure limits.

states at threshold worsens the agreement with the measured rate coefficients, although the high temperature (1150 K) results are perhaps equally well reproduced with and without scaling the harmonic frequencies.

We note that the present procedure of scaling the harmonic frequencies to approximate the effect of anharmonicity at the dissociation threshold does a poor job describing the density of states at intermediate and low energies and therefore introduces some additional error into the falloff calculations in Figures 12–14. This error is mitigated somewhat as the high pressure limiting rate coefficients are not affected by this scaling. Despite these qualifications, these results suggest that errors in calculating the density of states using the RRHO approximation can be more significant than errors in the energy transfer models or in α at intermediate and low pressures. Furthermore, it is not clear from the present comparisons with experimental rate coefficients for He, Ar, and CH_4 whether or not such an adjustment systematically improves the predicted rate coefficients.

Overall, agreement between the predicted and measured rate coefficients is good (equally so, with or without correcting for anharmonicity), demonstrating the predictive usefulness of the present energy transfer models and of trajectory-based calculations of energy transfer parameters. Likewise, the present results confirm the accuracy of the recommended experimental values,⁶⁶ with the possible exception of the falloff rate coefficients for $M = \text{Ar}$, where the recommended and experimental values are somewhat higher than the theoretical rate coefficients. We note that Golden¹⁹ recently discussed difficulties consistently modeling the experimental results for Ar using the ME and empirical values for α .

IV. CONCLUSIONS

Energy transfer in highly vibrationally excited CH_4 for eight baths was studied using classical trajectories. Direct dynamics calculations were carried out using validated, full-dimensional MP2 potential energy surfaces for $M = \text{He, Ne, H}_2$, and CH_4 . These results were used to test the accuracy of representing the interaction potential as a separable sum of pairwise interactions. For atomic baths, this approximation was found to be very accurate so long as an exponential form was used to describe the repulsive wall. The use of a Lennard-Jones interaction potential led to significant errors in the theoretical predictions, overpredicting energy transfer averages by up to a factor of 3. For diatomic baths, the separable pairwise approximation was not flexible enough to describe the dependence of the interaction potential on the orientation of the bath gas. The resulting ambiguity in the fitted parameters contributed an additional uncertainty of 10–50% to the predicted energy transfer averages. The separable pairwise approximation has been used in almost every study of energy transfer in the literature, and the present results suggest that such an approach may not be suitable for quantitative predictions for some systems.

A sampling scheme for using a single ensemble of trajectories to calculate energy transfer properties for a range of bath gas temperatures was introduced for atomic baths. The multitemperature sampling was shown to give more precise averages over a broader range of temperatures than the single temperature ensembles, for a fixed total number of trajectories. More generally, the use of small ensembles of only several hundreds of direct dynamics trajectories (as suggested by Lim and Gilbert⁵¹) has been shown to provide results accurate enough for parametrizing energy transfer models for use in ME calculations.

In addition to considering per collision energy transfer averages, we discussed first order energy transfer rate coefficients. These rate coefficients are straightforward to calculate using ensembles of trajectories yet avoid the customary but often arbitrary scaling to Lennard-Jones collision rates. It was confirmed that the energy transfer rate coefficients more directly predict the kinetic effect of the bath gases. Furthermore, the energy transfer rate coefficients may be more useful in rationalizing trends in the relative energy transfer efficiencies due to properties of the baths.

The temperature dependence of the average energy transferred in deactivating collisions $\alpha \equiv \langle \Delta E_d \rangle$ for eight baths was discussed. This quantity is often used to parametrize models of energy transfer assuming the functional form in eq 1. The present results suggest a more complicated temperature dependence, particularly at low temperature. Furthermore, it was shown that the relative bath gas efficiencies change as a function of

temperature. Together, these results suggest that relative room temperature values for α may not be directly useful in parametrizing energy transfer models intended for higher temperature applications, such as combustion processes.

Fully predictive (i.e., parameter-free) decomposition and association rate coefficients for CH_4 were calculated for all eight baths using the calculated values of α and the simple model for energy transfer outlined in assumptions 1–3 from the Introduction. Comparisons of the predicted rate coefficients were made with available experimental results for $\text{M} = \text{He}, \text{Ar}, \text{Kr},$ and CH_4 . In general, the agreement between the predicted and experimental rate coefficients is excellent and is within the recommended factor of 2 experimental uncertainties. The good agreement validates both the simplified energy transfer models used in the ME calculations for these systems and the trajectory based determinations of the energy transfer parameters. We note that these results should not be interpreted to imply that the physics neglected in assumptions 1–3 is not real. The overwhelming evidence is that the energy transfer function has explicit, nonseparable dependencies on the initial rotational state and vibrational energy of the target and has a long tail. Instead, the present work demonstrates that accurate rate coefficients can be obtained for some systems using the present simple energy transfer models *despite* assumptions 1–3. This conclusion is further supported by numerous recent kinetics calculations where the predictions made using the present energy transfer models and empirical values of α were found to agree well with a wide variety of experimental results. Clearly, one may identify systems where these assumptions will introduce error in the predicted kinetics, and continued effort identifying the limits of the present assumptions is needed. The present work is therefore complementary to detailed classical trajectory studies of energy transfer carried out by others designed to elucidate more clearly the underlying physics of energy transfer. Understanding when more complicated energy transfer functions are required and when the simpler schemes may be used with confidence are important areas of ongoing research.

Finally, we noted that the present low pressure calculations may suffer uncertainties of close to a factor of 2 due to our present neglect of anharmonicity when calculating the density of states for CH_4 . These uncertainties may be larger than the uncertainties associated with the energy transfer models and direct-trajectory-based parametrizations. Further progress toward predictive unimolecular kinetics will likely require anharmonic treatments for the density of states, such as the spectroscopic series approaches recently advocated by Nguyen and Barker⁶⁸ or the more approximate schemes of Troe and Ushankov⁷² and Schmatz.⁶⁹

■ ASSOCIATED CONTENT

S Supporting Information. Fitted intermolecular potential energy surface parameters and figures comparing QCISD(T)/CBS interaction energies with several low-level direct dynamics and approximate potential energy surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ajasper@sandia.gov

■ ACKNOWLEDGMENT

Helpful conversations with Joe Michael are gratefully acknowledged. This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy and as part of the Argonne-Sandia Consortium on High Pressure Combustion Chemistry. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94-AL85000. J.A.M. was supported in part by the Combustion EFRC, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC001198.

■ REFERENCES

- (1) Troe, J. J. *Chem. Phys.* **1977**, *66* (4745), 4758.
- (2) Barker, J. R.; Golden, D. M. *Chem. Rev.* **2003**, *103*, 4577.
- (3) Pilling, M. J.; Robertson, S. H. *Annu. Rev. Phys. Chem.* **2003**, *54*, 245.
- (4) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2006**, *110*, 10528.
- (5) Fernandez-Ramos, A.; Miller, J. A.; Klippenstein, S. J.; Truhlar, D. G. *Chem. Rev.* **2006**, *106*, 4518.
- (6) Smith, S. C.; Gilbert, R. G. *Int. J. Chem. Kinet.* **1988**, *20*, 307.
- (7) Miller, J. A.; Klippenstein, S. J.; Raffy, C. J. *J. Phys. Chem. A* **2002**, *106*, 4904.
- (8) Brown, N. J.; Miller, J. A. *J. Chem. Phys.* **1984**, *80*, 5568.
- (9) Gelb, A. J. *Phys. Chem.* **1985**, *89*, 4189.
- (10) Jasper, A. W.; Miller, J. A. *J. Phys. Chem. A* **2009**, *113*, 5612.
- (11) Barker, J. R.; Weston, R. E. *J. Phys. Chem. A* **2010**, *114*, 10619.
- (12) Bruehl, M.; Schatz, G. C. *J. Phys. Chem.* **1988**, *92*, 7223.
- (13) Lendvay, G.; Schatz, G. C. *J. Phys. Chem.* **1991**, *95*, 8748.
- (14) Lenzer, T.; Luther, K.; Troe, J.; Gilbert, R. G.; Lim, K. F. *J. Chem. Phys.* **1995**, *103*, 626.
- (15) Tardy, D. C.; Rabinovitch, B. S. *Chem. Rev.* **1977**, *77*, 369.
- (16) Barker, J. R. *J. Phys. Chem.* **1984**, *88*, 11.
- (17) Flynn, G. W.; Parmenter, C. S.; Wodtke, A. M. *J. Phys. Chem.* **1996**, *100*, 12817.
- (18) Lenzer, T.; Luther, K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 955.
- (19) Golden, D. M. *Int. J. Chem. Kinet.* **2008**, *41*, 245.
- (20) Sellevåg, S. R.; Georgievskii, Y.; Miller, J. A. *J. Phys. Chem. A* **2008**, *112*, 5095.
- (21) Kiefer, J. H.; Santhanam, S.; Srinivasan, N. K.; Tranter, R. S.; Klippenstein, S. J.; Oehlschlaeger, M. A. *Proc. Combust. Inst.* **2005**, *30*, 1129.
- (22) Yang, X.; Jasper, A. W.; Kiefer, J. H.; Tranter, R. S. *J. Phys. Chem. A* **2009**, *113*, 8318.
- (23) Gilbert, R. G. *Int. Rev. Phys. Chem.* **1991**, *10*, 319.
- (24) Clarke, D. L.; Oref, I.; Gilbert, R. G.; Lim, K. F. *J. Chem. Phys.* **1992**, *96*, 5983.
- (25) Linhananta, A.; Lim, K. F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1385.
- (26) Yerram, M. L.; Brenner, J. D.; King, K. D.; Barker, J. R. *J. Phys. Chem.* **1990**, *94*, 6341.
- (27) Michael, J. V.; Su, M.-C.; Sutherland, J. W.; Carroll, J. J.; Wagner, A. F. *J. Phys. Chem. A* **2002**, *106*, 5297.
- (28) Feng, Y.; Niiranen, J. T.; Bencsura, Á.; Knyazev, Gutman, D.; Tsang, W. J. *J. Phys. Chem.* **1993**, *97*, 871.
- (29) Harding, L. B.; Georgievskii, Y.; Klippenstein, S. J. *J. Phys. Chem. A* **2005**, *109*, 4646.
- (30) *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, <http://webbook.nist.gov>.
- (31) Medvedev, D. M.; Harding, L. B.; Gray, S. K. *Mol. Phys.* **2006**, *104*, 73.

- (32) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; pp 1110 and 1212.
- (33) Kee, R. J.; Dixon-Lewis, G.; Warnatz, J.; Coltrin, M. E.; Miller, J. A. A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties. *Sandia Technical Report SAND86-8246*, 1986.
- (34) Klippenstein, S. J.; Wagner, A. F.; Dunbar, R. C.; Wardlaw, D. M.; Robertson, S. H.; Miller, J. A. *VariFlex*, version 2.0; Argonne National Laboratory, Argonne, IL, 2006.
- (35) DelBene, J. E. *J. Phys. Chem.* **1993**, *97*, 107.
- (36) Gordon, M. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5412.
- (37) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.
- (38) Alexander, W. A.; Troya, D. *J. Phys. Chem. A* **2006**, *110*, 10834.
- (39) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 1992; p 21.
- (40) Hack, M. D.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *110*, 4315. fit the data of Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1965**, *43*, 2429.
- (41) Le Roy, R. J.; Huang, Y.; Jary, C. *J. Chem. Phys.* **2006**, *125*, 164310.
- (42) Krupenie, P.; Weissman, S. *J. Chem. Phys.* **1965**, *43*, 1529.
- (43) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397; **1964**, *40*, 2047, 2474, 2480, 2745.
- (44) Slater, J. C.; Koster, G. F. *Phys. Rev.* **1954**, *94*, 1498.
- (45) Wang, Y.; Mak, C. H. *Chem. Phys. Lett.* **1995**, *235*, 37.
- (46) Liu, T.; Truhlar, D. G. *TB*, version 1.0.1; University of Minnesota: Minnesota, 2004; see comp.chem.umn.edu/tbpac. Liu, T. *Ph.D. Thesis*, University of Minnesota, 2000.
- (47) Andersen, H. C. *J. Chem. Phys.* **1980**, *72*, 2348.
- (48) Faist, M. B.; Muckerman, J. T.; Schubert, F. E. *J. Chem. Phys.* **1978**, *69*, 4087.
- (49) Efron, B. *Ann. Stat.* **1979**, *7*, 1.
- (50) Nangia, S.; Jasper, A. W.; Miller, T. F., III; Truhlar, D. G. *J. Chem. Phys.* **2004**, *120*, 3586.
- (51) Lim, K. F.; Gilbert, R. G. *J. Phys. Chem.* **1990**, *94* (72), 77.
- (52) Jasper, A. W.; Oana, C. M.; Truhlar, D. G. *DiNT*, version 1.0; Sandia National Laboratories and University of Minnesota: California and Minnesota, 2010; see www.sandia.gov/~ajasper/dint.
- (53) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO*, version 2006.1; see www.molpro.net.
- (54) Lenzer, T.; Luther, K. *J. Chem. Phys.* **1996**, *105*, 10944.
- (55) Meroueh, O.; Hase, W. L. *J. Phys. Chem. A* **1999**, *103*, 3981.
- (56) Brunsvold, A. L.; Garton, D. J.; Minton, T. K.; Troya, D.; Schatz, G. C. *J. Chem. Phys.* **2004**, *121*, 11702.
- (57) Fletcher, F. J.; Rabinovitch, B. S.; Watkins, K. W.; Locker, D. J. *J. Phys. Chem.* **1966**, *70*, 2823.
- (58) Ahumada, J. J.; Michael, J. V.; Osborne, D. T. *J. Chem. Phys.* **1972**, *57*, 3736.
- (59) Michael, J. V.; Osborne, D. T.; Suess, G. N. *J. Chem. Phys.* **1972**, *58*, 2800.
- (60) Michael, J. V.; Payne, W. A.; Whytock, D. A. *J. Chem. Phys.* **1976**, *65*, 4830. Whytock, A. D.; Michael, J. V.; Payne, W. A. *Chem. Phys. Lett.* **1976**, *42*, 466.
- (61) Hartig, R.; Troe, J.; Wagner, H. G. *Symp. Int. Combust. Proc.* **1971**, *13*, 147.
- (62) Davidson, D. F.; DiRosa, M. D.; Chang, A. Y.; Hanson, R. K.; Bowman, C. T. *Symp. Int. Combust. Proc.* **1992**, *24*, 589. Davidson, D. F.; Hanson, R. K.; Bowman, C. T. *Int. J. Chem. Kinet.* **1995**, *27*, 305.
- (63) Kiefer, J. H.; Kumaran, S. S. *J. Phys. Chem.* **1993**, *97*, 414.
- (64) Koike, T.; Kudo, M.; Yamada, H. *Int. J. Chem. Kinet.* **2000**, *32*, 1.
- (65) Sutherland, J. W.; Su, M.-C.; Michael, J. V. *Int. J. Chem. Kinet.* **2001**, *33*, 669.
- (66) Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. *Phys. Chem. Ref. Data* **2005**, *34*, 757.
- (67) Barnes, R. W.; Pratt, G. L.; Wood, S. W. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 229.
- (68) Nguyen, T. L.; Barker, J. R. *J. Phys. Chem. A* **2010**, *114*, 3718.
- (69) Schmatz, S. *Chem. Phys.* **2008**, *346*, 198.
- (70) Chen, C. J.; Back, M. H.; Back, A. R. *Can. J. Chem.* **1975**, *53*, 3580.
- (71) Brouard, M.; Macpherson, M. T.; Pilling, M. J.; Tulloch, J. M.; Williamson, A. P. *Chem. Phys. Lett.* **1985**, *113*, 413. Brouard, M.; Macpherson, M. T.; Pilling, J. *Phys. Chem.* **1989**, *93*, 4047.
- (72) Troe, J.; Ushakov, V. G. *J. Phys. Chem. A* **2009**, *113*, 3940.